New organic metals based on sulphur heterocycles.

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NEW ORGANIC METALS BASED ON SULPHUR HETEROCYCLES

by

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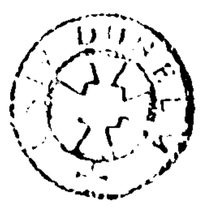

DECLARATION

The work described in this thesis was carried out by the author. in the Department of Chemistry, University of Durham, between October 1986 and September 1989. It has not been submitted previously for a degree at this, or any other, University.

MEMORANDUM

For Mum, Dad and Yvonne

With Love

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ABSTRACT

NEW ORGANIC METALS BASED ON SULPHUR HETEROCYCLES

Novel 1,3-dithiole and 1-selena-3-thiole Wittig-Horner reagents have been developed and used in the efficient synthesis of a range of new symmetrical and unsymmetrical extended tetrathiafulvalene, selenatrithiafulvalene and diselenadithiafulvalene derivatives. Cyclic voltammetry establishes that these π-donor molecules each undergo a two-electron oxidation process to yield the dication. Complexation with 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) demonstrates the suitability of these extended donors in the field of conducting charge-transfer complexes. X-ray analysis of bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (127) reveals a highly distorted structure. However, the donor adopts a very different conformation when complexed with TCNQ, as a 1:4 charge-transfer complex, which is highly conducting, σ(rt) = 60 S cm^{-1}. Extended bis(1,3-dithiolium) dications have been prepared and found to form semi-conducting charge-transfer complexes by metathesis reaction with lithium-TCNQ.

The synthesis of monosubstituted tetrathiafulvalene (TTF) amphiphiles suitable for Langmuir-Blodgett film formation has been accomplished. Stable, high-quality multilayers of 4-(carbohexadecoxy)-tetrathiafulvalene (190) and 4-(thiocarbohexadecoxy)tetrathiafulvalene (191) have been found to be highly conducting after iodine doping, σ(rt) ~ 1 S cm^{-1}.

Salts of a range of cyclic sulphonium cations, *eg*. 1-methyl-1,4-dithiacyclohexanium cation, with TCNQ (1:2 stoichiometry) have been prepared and characterised in the solid-state by X-ray analysis, variable-temperature conductivity data and magnetic susceptibility measurements.

Adrian Jerome Moore (December 1989)

CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 "ORGANIC METALS"

The large majority of organic solids are electrical insulators with room temperature conductivities (σ_{rt}) in the range 10^{-9} to 10^{-20} S cm^{-1}. Until recently, the idea[1] that such a traditional organic material could exhibit the electrical, optical and magnetic properties characteristic of a metal seemed to be a complete contradiction in terms. The picture has, however, dramatically changed in recent years, as research on organic conductors has now given rise to new classes of molecular and polymeric materials with properties analogous to those of metals. In only two decades there has been a revolution in terms of electrical conductivity, with a progression from insulating and semiconducting behaviour to superconductivity, and a new field of study has emerged at the interface of chemistry, physics and materials science, known as "organic metals" [2].

This thesis concerns the study of charge-transfer (C-T) complexes, which comprise one of three major classes of organic metals - the other classes are conducting polymeric systems[3] and organometallic complexes[4].

1.2 THEORY OF CONDUCTIVITY IN ORGANIC METALS

1.2.1 Background

The theory of conductivity in organic metals is marked by many points of contention, but, in a general sense, the features that distinguish organic metals, semiconductors and insulators are just those that are operative for standard inorganics *ie.* the conduction properties depend on the nature of the electronic energy bands in these solids. The organics are somewhat atypical in that conductivity is often

associated with a preferred direction by several orders of magnitude. This anisotropy is often so pronounced that many organic metals are termed one-dimensional (1-D) metals.

1.2.2 Band Theory of Solids

When a large number of atoms, or molecules, are brought together to form a polymeric chain, or a crystalline solid, an energy band forms. resulting from the delocalisation of the molecular orbitals of the individual components throughout the system. Some representative band schemes are shown in Figure 1.1.

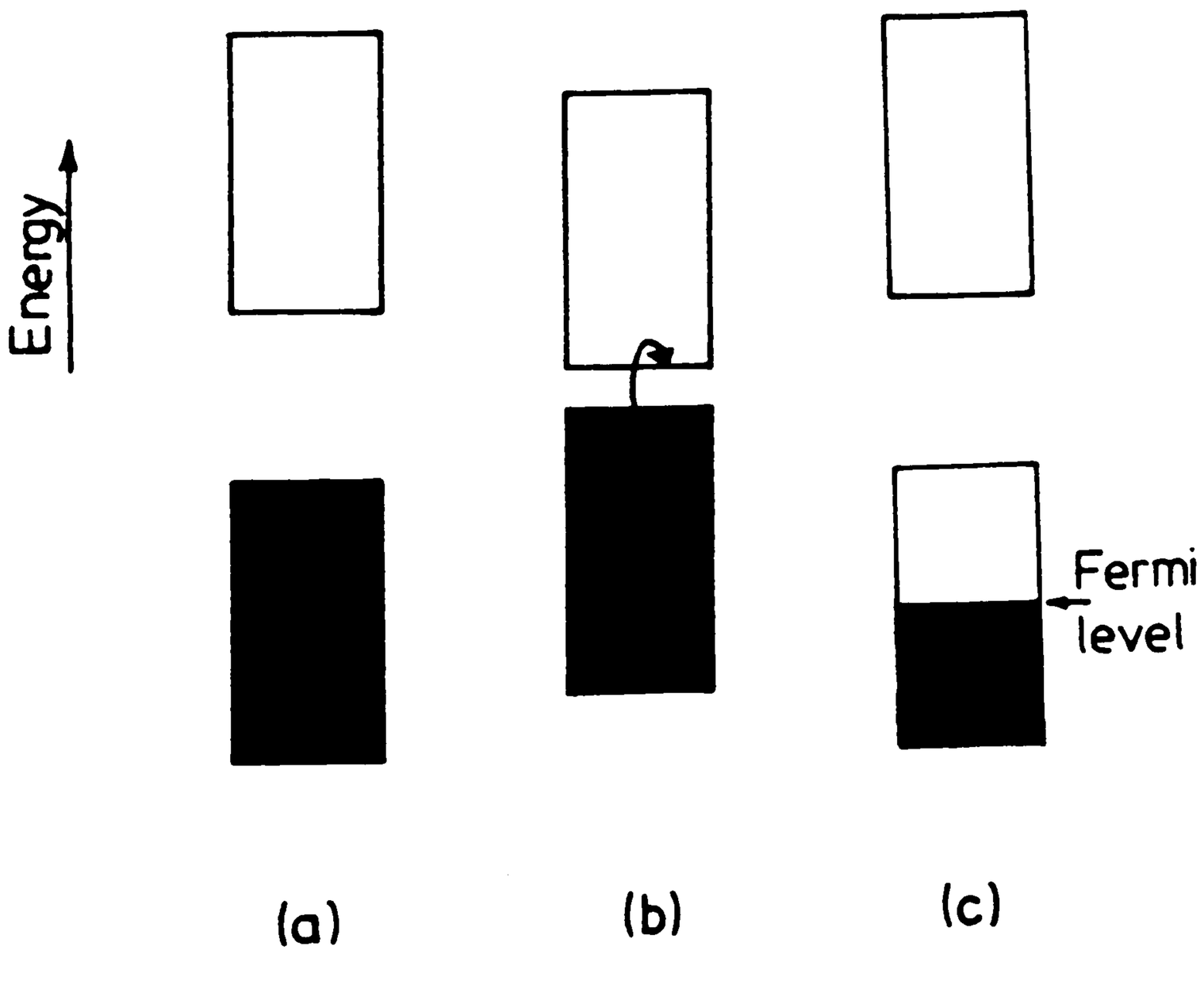


Figure 1.1: *Schematic representation of band filling in (a) insulators; (b) semiconductors and (c) metals. The shaded areas represent electronic states occupied by electrons.*

The formation of energy bands in itself does not automatically imply metallic properties; the additional pre-requisite is the occupancy of

these energy bands. When the energy gap (E_g) between the highest occupied band (the Fermi level) and the lowest unoccupied band (the conduction band) is large (Figure 1.1a), electrons cannot be promoted into the conduction band by the application of a small potential difference. The system is thus electrically insulating. As the energy gap decreases (Figure 1.1b), thermal excitation of electrons from the Fermi level to the conduction band becomes possible, and the material may behave as a semiconductor. Consequently, the chief characteristic of a semiconductor is the requirement of thermally activated conductivity. This is reflected by an increase in conductivity with an increase in temperature. When the gap between the bands becomes vanishingly small (Figure 1.1c), the material behaves as a metal.

Metallic behaviour is associated with partially filled energy bands, in which it is possible for a large number of electrons to move easily, on application of a small potential difference, into higher conducting energy states within the band. Unlike semiconductors, there is no band gap in metals, and therefore the temperature dependence of the conductivity is dominated by the mobility of the charge carriers; this depends on the scattering of the conducting electrons by interactions with the lattice vibrations (termed *phonons*). As the temperature is reduced, the amplitude of the lattice vibrations is diminished and the mobility, and hence conductivity, increases.

1.2.3 Conductivity in One-Dimensional Metals

Electrical conductivity in 1-D metals may be understood in terms of the simple band theory outlined above. However, the physics of a 1-D system is dramatically different from that found in a three-dimensional (3-D) material, this difference being at the heart of the study of

organic metals.

The behaviour of 1-D metals was first discussed in 1955, when Peierls pointed out that, at low temperatures, a 1-D metal could not maintain long-range order, and would be unstable with respect to lattice distortions[5]. These Peierls distortions are analogous to the familiar Jahn-Teller distortions. The driving force towards such distortion is the electronic stability gained from the splitting of the conduction band into a fully occupied band of lower energy and an empty band of higher energy (Figure 1.2). The emergence of a band gap, as a result of the structural changes associated with a Peierls distortion, often results in a transition from a metallic into a semiconducting, or even insulating, ground state.

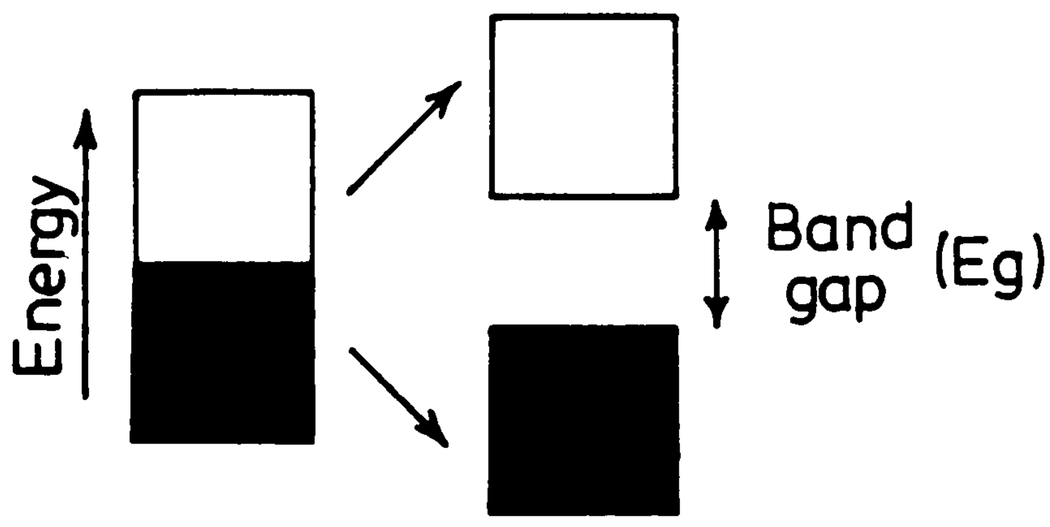


Figure 1.2: *Band splitting - the effect of Peierls distortion on energy levels.*

Peierls distortions lead to a localisation of the conducting electrons and formation of an associated charge density wave (CDW) (Figure 1.3). The periodicity of the distortion is determined by the nature of the partially filled energy bands. A half-filled band provides the simplest example, and is also the most energetically favourable for such a transition, as it is commensurate with the lattice, which results in dimerisation or doubling of the unit cell. Conductivity resulting from translation of the CDW is prevented by a

potential energy barrier, represented by the band gap. E_g (Figure 1.2). Consequently, the CDW is "pinned" to the underlying lattice. giving rise to an insulator. In an incommensurate system, the CDW will not be locked to the lattice and will be free to translate to new positions without adversely affecting the energetics of the system: hence. a mechanism for high conductivity exists. Consequently, an impurity-free. truly incommensurate system should be superconducting[7]: this exciting prospect has provided a major incentive for the study of all aspects of organic metals.

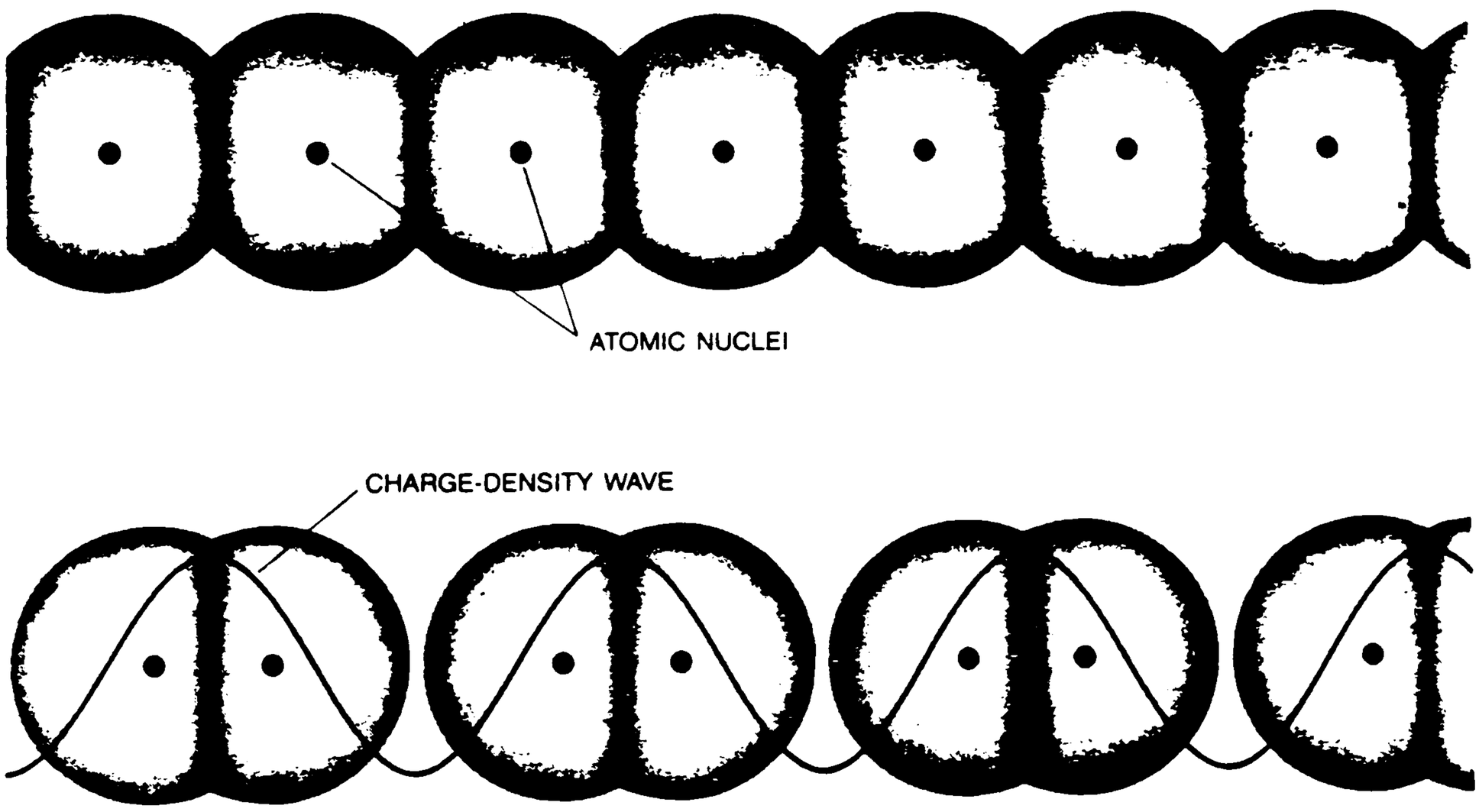


Figure 1.3: *Peierls distortion within a linear array of atoms and the associated charge density wave (CDW).*

In a strictly 1-D system, Peierls distortions may only occur at absolute zero. However, C-T complexes are 3-D crystals rather than single chain filaments and there are, therefore, interchain interactions present to some extent. These give rise to 3-D ordering and force the distortions to occur at a finite temperature, typically between 20 and

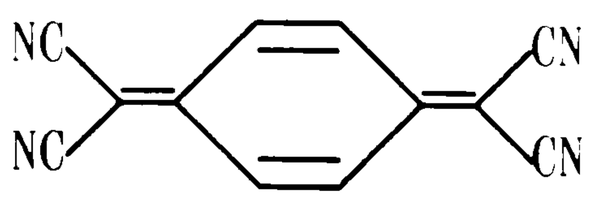
100 K. The energy gained upon distortion is less favourable in the incommensurate state than the commensurate, and hence the phase transition of the former occurs at lower temperatures. Suppression of this transition in order to retain the metallic state at near absolute zero has been a major achievement of the 1980's.

It should be stressed that the theory of conduction in organic metals is continually being updated, and that the picture represented here is simplistic. A far more comprehensive discussion of the topic may be found in numerous specialist papers[8].

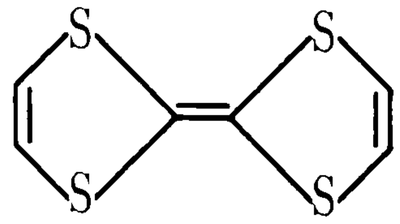
1.3 CHARGE-TRANSFER COMPLEXES AS ORGANIC METALS

1.3.1 Introduction

A stable C-T complex is usually formed by the transfer of an electron from a donor (D) to an acceptor (A) molecule[9]. The possibility that such C-T complexes could exhibit metallic properties was suggested as long ago as 1913[1]. This postulate was first realised in 1954, when the first highly conducting organic material, an unstable perylene-$(bromine)_x$ complex ($\sigma_{rt} \sim 1$ S cm^{-1}), was reported[10]. While this finding may be considered as a major landmark, a real burst in research on organic conductors did not occur until after the discovery of the powerful electron acceptor, 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) (1)[11]. In the early 1960's, TCNQ was found to form stable ion-radical salts with a variety of organic cations[12]. The majority of these salts exhibit semiconductor behaviour ($\sigma_{rt} = 10^{-2} - 10^{-5}$ S cm^{-1}); quinolinium-$(TCNQ)_2$ provides a notable exception, having high conductivity (σ_{rt} = 100 S cm^{-1}) indicative of metallic behaviour.



(1)



(2)

Almost a decade later, the electron donor tetrathiafulvalene (TTF) (2) was synthesised[13]. This compound, like TCNQ, formed stable ion-radical salts (*eg.* TTF-$Cl_{0.6}$, σ_{rt} ~ 0.2 S cm^{-1})[14]. It was not long after this that organic metals were truly born with the marriage of TTF and TCNQ[15]. The resultant 1:1 complex was metallic, σ_{rt} ~ 500 S cm^{-1}, the conductivity rising to a maximum of 1 x 10^4 S cm^{-1} at 59K. This archetypal material will now be considered briefly to illustrate the properties of a typical 1-D metal, before more recent advances are reviewed.

1.3.2 TTF-TCNQ: The Archetypal Organic Metal

TTF-TCNQ displays the classical structural, electrical, magnetic and optical properties of an organic metal. Both TTF and TCNQ are planar molecules (D_{2h} symmetry), of similar size and with π-delocalisation extending throughout the molecule. The X-ray structure of the complex (Figure 1.4) reveals segregated stacks of donor and acceptor, each running parallel to the crystallographic b-axis (referred to as the stacking axis)[16].

This mode of crystal packing contrasts markedly with the alternating donor-acceptor arrangements observed within stacks of most C-T complexes; these are inherently insulating. The molecular planes of the TTF and TCNQ molecules are tilted with respect to the stacking axis, having opposite tilts with respect to each other: this gives rise to the so-called "herringbone" structure. Within the stacks, both donor and acceptor stack uniformly; that is, each molecule is equidistant from its

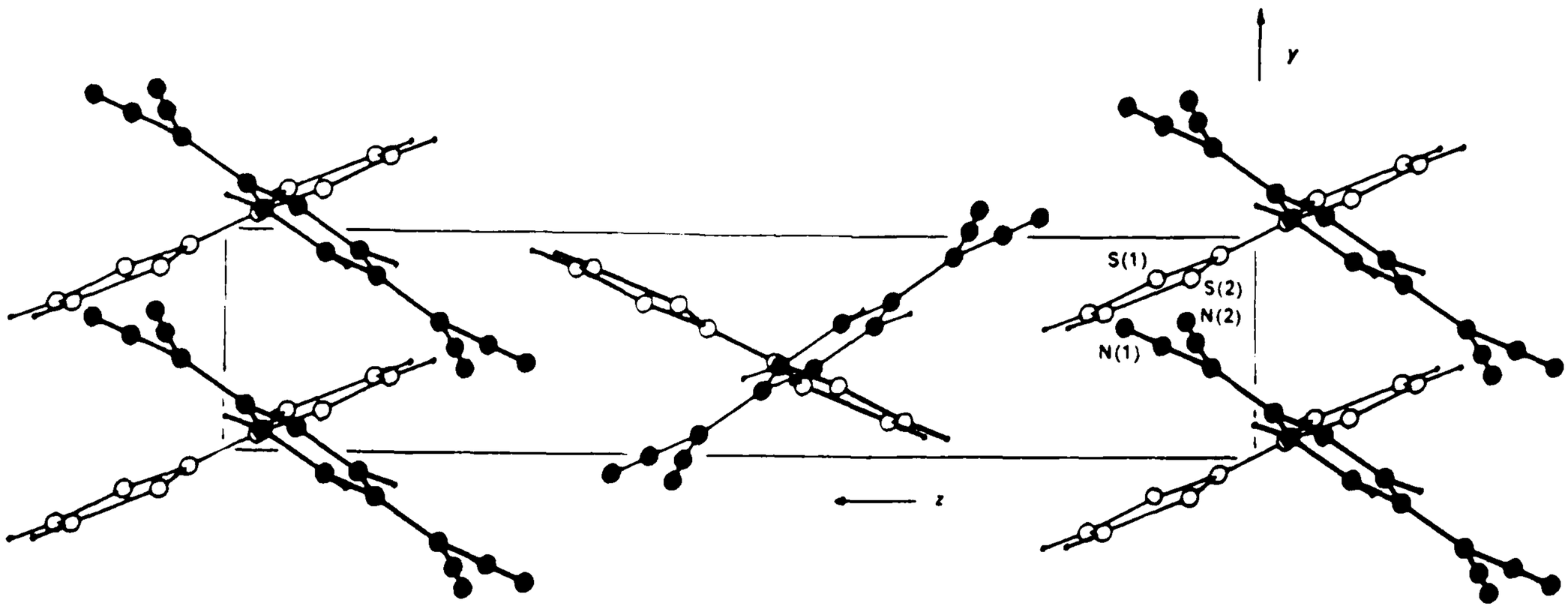


Figure 1.4: *X-ray structure of TTF-TCNQ.*

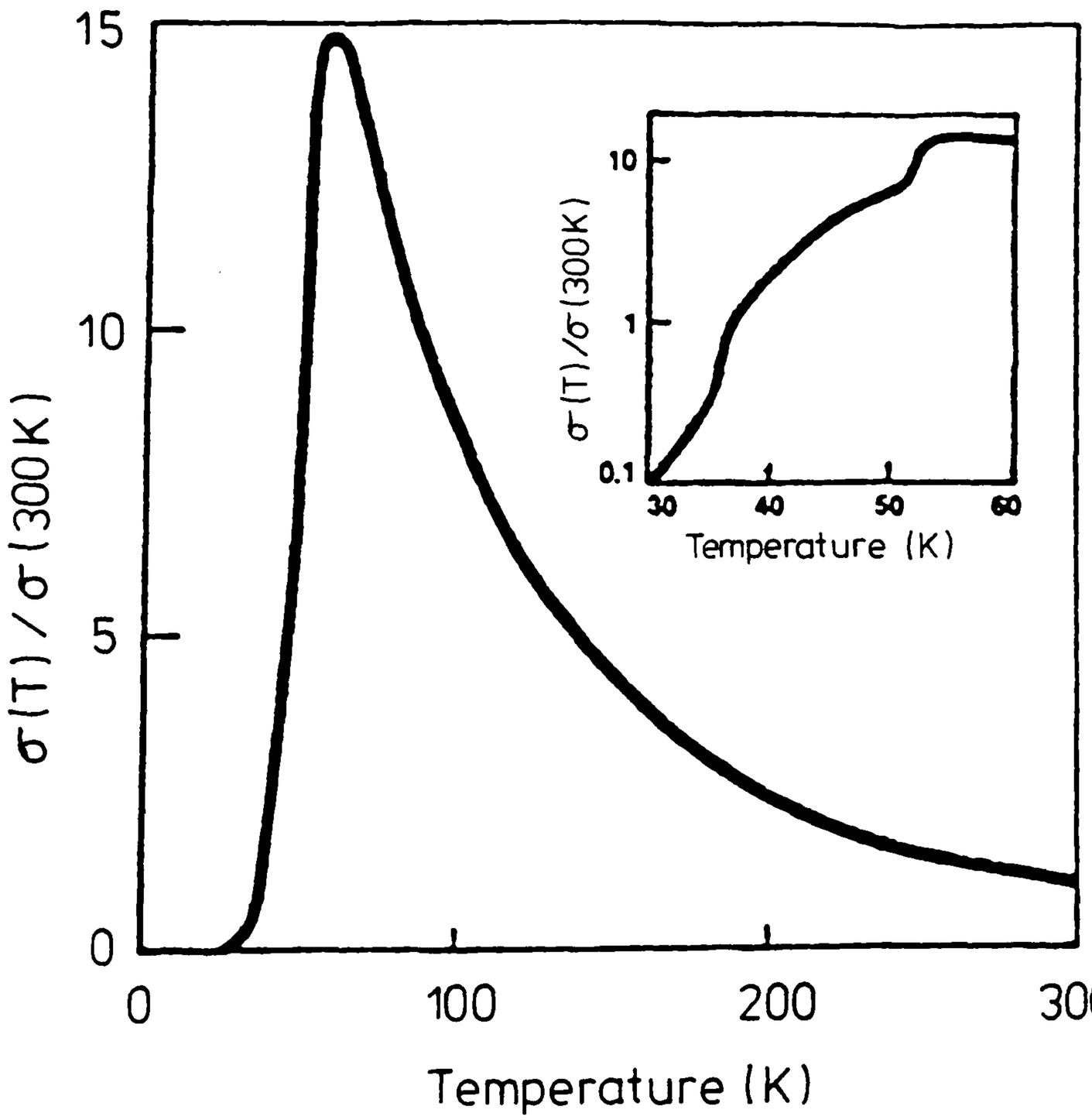


Figure 1.5: *Conductivity of TTF-TCNQ as a function of temperature; Inset: phase transitions observed between 60 and 30K.*

neighbours in the stack. Any dimerisation or non-uniformity along a stack tends to lead to semiconducting behaviour. Furthermore, adjacent molecules do not lie directly above one another, but are shifted such that the exocyclic bond of one molecule lies over the ring of its neighbour. The net result of these two facts is strong *intra*stack delocalisation and only weak *inter*stack interactions. Thus, highly anisotropic conduction arises with conductivity over 500 times greater along the stacking axis than along either the crystallographic a- or c-axes. On cooling, the conductivity of TTF-TCNQ shows typical metallic behaviour, rising 20-fold from *ca.* 500 S cm^{-1} at room temperature to over 1 x 10^4 S cm^{-1} at 59K (Figure 1.5). On further cooling, the complex undergoes three phase transitions at 53, 47 and 38K (Figure 1.5, inset), leading to an insulating state. These transitions have been investigated by X-ray and neutron scattering and have been attributed to Peierls distortions within, and across, the individual stacks resulting in a fully 3-D system.

The degree of charge transfer (ρ) from TTF to TCNQ is 0.59 electrons per molecule; this is based upon diffuse X-ray scattering techniques[17] and infrared spectroscopy[18]. Thus, there is a partially-filled conduction band and a CDW which is incommensurate with the underlying lattice. High conductivity is, therefore, attainable. Work on the TTF-bromide system dramatically illustrates the importance of incomplete charge-transfer in these highly conducting organic solids. A bromide-deficient salt ($TTF\text{-}Br_{0.71}$) has room temperature conductivity comparable to that of TTF-TCNQ; a stoichiometric 1:1 salt, prepared electrochemically, is thirteen orders of magnitude less conducting (Table 1.1)[19]. Thus, partial charge-transfer may be achieved in one of two ways: either by delicately balancing the ionisation potential of the donor with the electron affinity of the acceptor, as for TTF-TCNQ, or by

formation of a complex of stoichiometry other than 1:1.

COMPLEX	ρ	σ(rt) (S cm^{-1})‡
TTF-TCNQ	0.59	500
TTF-Br$_{0.71}$	0.71	200
TTF-Br	1.00	1 x 10^{-11}

Table 1.1: *Room temperature conductivities of several TTF salts: dependence on degree of charge-transfer (ρ); ‡single crystal, four-probe measurement.*

1.3.3 The Design of New Conducting C-T Complexes

In summary, the attainment of the metallic state in C-T complexes is the result of a delicate balance of many factors, some of which are outlined below:

(1) one, or both, of the donor and acceptor should be planar, or nearly planar.

(2) one, or both, of the donor and acceptor requires π-delocalised orbitals.

(3) the crystal structures must be highly ordered - this is favoured by symmetrical donors and acceptors.

(4) the donor and acceptor should form segregated stacks in the crystal.

(5) there must be a partially filled energy band.

(6) the free radical salt of one, or both, components should be stable.

(7) the redox potentials of donor and acceptor must be closely matched.

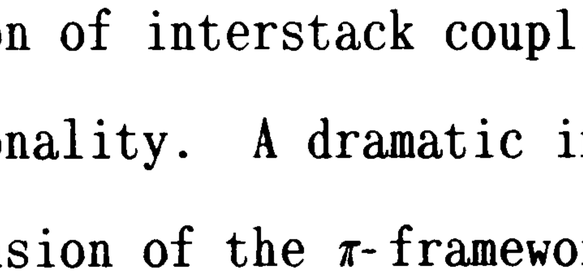
Considerable research effort has been directed towards the synthesis of new donors and acceptors following these guidelines; one of the major rewards being the attainment of organic superconductivity. Notable landmarks will now be reviewed.

1.4 NEW ELECTRON DONORS

1.4.1 Systematic Modifications to TTF

TTF (2) represents a prototype structure, ripe for structural and elemental modifications, that has provided a fertile ground for synthetic chemists to explore new methodologies. A plethora of new TTF analogues now exist, the synthetic routes to which have been regularly reviewed[20].

The initial structural modifications to TTF involved extending the σ-bond framework by alkyl substitution, the result being a reduction of the oxidation potential of the donor. For example, symmetrically substituted derivatives, tetramethyl-TTF (TMTTF) (3)[21] and hexamethylene-TTF (HMTTF) (4)[22] were prepared, whose TCNQ complexes are metallic (σ_{rt} = 200 - 500 S cm^{-1}). On cooling, metal-insulator (M-I) transitions occur at temperatures above that for TTF-TCNQ. This was explained by a reduction of interstack coupling and a resultant increase of one-dimensionality. A dramatic increase occurs in the oxidation potential on extension of the π-framework of the basic TTF skeleton [*eg.* dibenzo-TTF (DBTTF) (5)[23], donor (6)[24]] or by introduction of electron withdrawing groups [for example compounds (7) and (8)][20a], and these donors tend to yield insulating, or at best semiconducting, complexes.

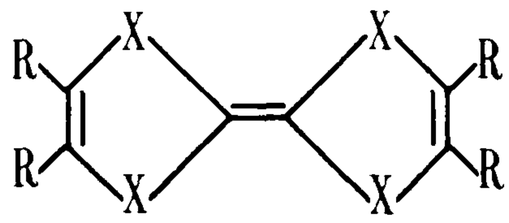


(2) $R_1 = R_2 = H$
(3) $R_1 = R_2 = Me$
(4) $R_1R_1 = R_2R_2 = -(CH_2)_3-$
(5) $R_1R_1 = R_2R_2 = -(CH=CH)_2-$
(6) $R_1 = Me$; $R_2R_2 = -(CH=CH)_2-$
(7) $R_1 = R_2 = CN$
(8) $R_1 = R_2 = CF_3$

The next logical step was the preparation of the larger chalcogen analogues of TTF. Three important trends can be expected to occur upon

replacement of sulphur with selenium or tellurium. The more diffuse 'p' and 'd' orbitals of the larger heteroatoms should give greater conduction bandwidths, due to increased intrastack π-interactions. In addition, this increase in orbital size ought to increase the interchain interactions giving rise to a more two-dimensional character, with a net suppression of the Peierls distortion. Finally, the greater polarisability of the larger heteroatoms should reduce the on-site Coulombic repulsion and help support doubly charged species. The anticipated effects of these trends were enhanced conductivity and stabilisation of the metallic state.

A large number of selenium containing analogues of TTF are now known[25]. In general, the TCNQ complexes of the tetraselenafulvalenes show increased stability of the metallic state compared with their TTF counterparts. For example, tetraselenafulvalene (TSeF) (9)-TCNQ (σ_{rt} ~ 800 S cm^{-1})[26] has a higher room temperature conductivity than TTF-TCNQ, and retains metallic behaviour to 40K[27], *ca.* 19K below the M-I transition found in TTF-TCNQ. Furthermore, it has been found that the donor stacks dominate the transport properties in TSeF-TCNQ derivatives, a consequence of increased intrastack π-interactions. Finally, the increased dimensionality of these derivatives may be exemplified by hexamethylene-TSeF (HMTSeF) (10)-TCNQ (σ_{rt} ~ 1500 S cm^{-1})[28]. On cooling, the conductivity rises 3-4 fold, reaching a broad maximum between 45 and 70K. On further cooling, the conductivity decreases but remains metallic to 1.1K. This smearing of the Peierls transition may be accounted for by strong interstack interactions, *viz.* HMTSeF-TCNQ displays four strong Se··N contacts.



(9) X=Se; R=H
(10) X=Se; RR=$-(CH_2)_3-$
(11) X=Te; RR=$-(CH_2)_3-$
(12) X=Te; RR=$-(CH{=}CH)_2-$
(13) X=Te; R=H
(16) X=Se; R=Me

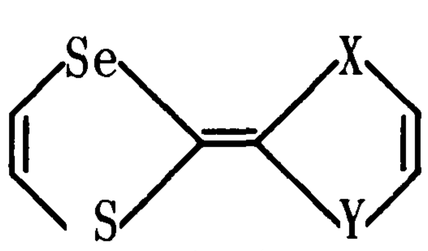
Tetratellurafulvalenes (TTeF's) have proved to be a formidable synthetic challenge. The first derivatives, hexamethylene-TTeF (HMTTeF) (11)[29] and dibenzo-TTeF (DBTTeF) (12)[30], were both reported in 1982, with the parent tetratellurafulvalene (TTeF) (13) having only recently been synthesised[31]. In general, the oxidation potentials of the tellurium compounds lie between those of the corresponding sulphur and selenium analogues *cf.* TTF < TTeF < TSeF. It has been proposed that ionisation is influenced by two factors which have opposite effects in the series S, Se, Te; these being, valence state ionisation potentials of the heteroatoms, and the differences in heteroatom-carbon orbital interactions[30]. In addition, the difference between the first and second ionisation potentials decreases along the series TTF > TSeF > TTeF, reflecting decreased intramolecular Coulombic repulsion energy of the dication in this series. Table 1.2 compares the properties of TTeF-TCNQ with its chalcogen analogues[32].

COMPLEX	σ(rt) [a] (S cm^{-1})	$\frac{\sigma(max)}{\sigma(rt)}$	ρ	T(max) (K)
TTF-TCNQ	500	14	0.59	59
TSeF-TCNQ	800	12	0.63	40
TTeF-TCNQ	1800	2	0.71	(100)[b]

Table 1.2: *Comparison of conductivity characteristics of TTeF-TCNQ with its earlier chalcogen analogues; a) single crystal, four-probe measurement; b) approximate value.*

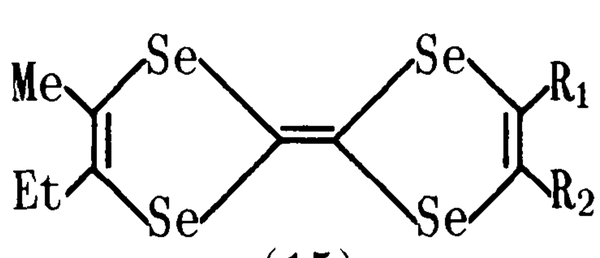
The room temperature conductivities tend to increase in the series TTF < TSeF < TTeF as a result of increased intrastack π-interactions (increased bandwidth). In all cases, the phase-transition is smeared in the TCNQ complexes of TTeF derivatives, suggesting that these have a greater two-dimensional character than their smaller chalcogen analogues. Detailed structure and transport property analysis of the TTeF-TCNQ's have been severely hampered due to crystal growth problems, and further results are eagerly awaited.

Introduction of disorder into the crystal structure successfully stabilises the metallic state. Although beneficial, it must be noted that disorder generates random potentials which may significantly hinder electron transport. The two donors (14) and (15) provide an interesting insight into the effect of disorder, as both have built-in static disorder in the form of *cis*/*trans* isomers.



(14)

cis: X=Se; Y=S
trans: X=S; Y=Se



(15)

cis: R_1=Me; R_2=Et
trans: R_1=Et; R_2=Me

In both cases, the conductivity as a function of temperature of their TCNQ complexes reflects metallic behaviour. Donor (14)-TCNQ shows a sharp M-I transition at 64K[27]. This complex has low symmetry, but is essentially isostructural with TTF-TCNQ and TSeF-TCNQ; as a result, the band structure is not significantly affected. More drastic disorder is introduced into the TCNQ complex of donor (15), with variable interstack interactions. The result is a smeared M-I transition at 28K [*cf.* tetramethyl-TSeF (TMTSeF) (16)-TCNQ, T_{MI} = 57K][33].

The composition of the donor and acceptor stacks may be systematically varied by doping with another donor, or acceptor, in a

disorder-inducing technique known as alloying. For example, introducing 10% methyl-TCNQ (MTCNQ) into TSeF-TCNQ blurs the phase transition at 28K and increases the conductivity at 4K by four orders of magnitude[34]. The alloying technique has been used to elucidate the source of observed phase transitions in a number of C-T complexes. For example, TTF-TCNQ has, as mentioned earlier, three distinct phase transitions. On doping with 5% TSeF, the transition at 38K is "washed out", providing the valuable information that this transition is mainly due to the donor stacks. Furthermore, the transition at 53K is completely unaffected by TSeF incorporation, indicating that it is dominated by the TCNQ stacks[27,35]. With the continuing advent of new tellurium containing donors, construction of binary and ternary alloys of the type $(TTeF)_x$-$(TSeF)_y(TTF)_{1-x-y}$ becomes an exciting possibility.

In summary, the goal of this brief review has been to outline key contributions in assembling useful guidelines for the design of new donors for organic metals based on TTF. These may be summarised as follows:

(1) Substitution of sulphur for a larger chalcogen increases σ(rt) - selenium incorporation also lowers the M-I transition.

(2) Increased dimensionality tends to eliminate the M-I transition.

(3) Introduction of disorder into a system results in a smearing of the phase transition.

(4) A decrease of intramolecular Coulombic repulsion stabilises the dicationic state.

These guidelines have been addressed in the synthesis of a vast panoply of new donors incorporating tetraheterofulvalenes substituted by alkyl, cycloalkyl, aryl, heteroalkyl and cycloheteroalkyl groups, as well as those incorporating more diverse structural arrangements (*eg.* cage compounds[36,37]). Finally, it should be stressed that whilst these points serve as guidelines for the design of new organic donors, the

crystal structure of the resultant complexes is ultimately crucial in determining transport properties.

1.4.2 Organic Superconductivity

The attainment of superconductivity is one of the most striking consequences of organic metals research. When certain materials are cooled below a critical temperature, T_c, their electrical resistance abruptly vanishes. In 1911, superconductivity was first observed in mercury (T_c = 4.2K)[38]. Since then, many other superconductors have been discovered, including metals, alloys, ceramics and the organic salts described here.

1.4.2.1 The Bechgaard Salts, $(TMTSeF)_2X$

The first superconducting organic compound, reported by Bechgaard and Jerome in 1980, was $(TMTSeF)_2PF_6$ [TMTSeF = tetramethyltetraselenafulvalene (16)], which showed pressure-induced superconductivity (T_c = 0.9K, 12 kbar)[39]. This result stimulated the preparation of a range of cation-radical salts, $(TMTSeF)_2X$, with inorganic anions (X), the so-called "Bechgaard salts". Under sufficiently large pressure, superconductivity has been observed and independently verified in the salts where X = PF_6^-, AsF_6^-, SbF_6^-, TaF_6^-, ReO_4^- and ClO_4^- [6,40]; $(TMTSeF)_2ClO_4$ is a notable example, being the only ambient pressure superconductor in the series (T_c = 1.3K, 1 bar)[41]. Superconductivity is not observed in the isostructural series $(TMTTF)_2X$.

Important features related to superconductivity in these materials lie in the crystal structures. The Bechgaard salts are all isostructural; the essentially planar TMTSeF molecules stack in a zig-zag

fashion, forming a 1-D chain, which parallels the axis of highest conductivity. The crystal structure of $(TMTSeF)_2BrO_4$ is representative of the whole series of salts (Figure 1.6).

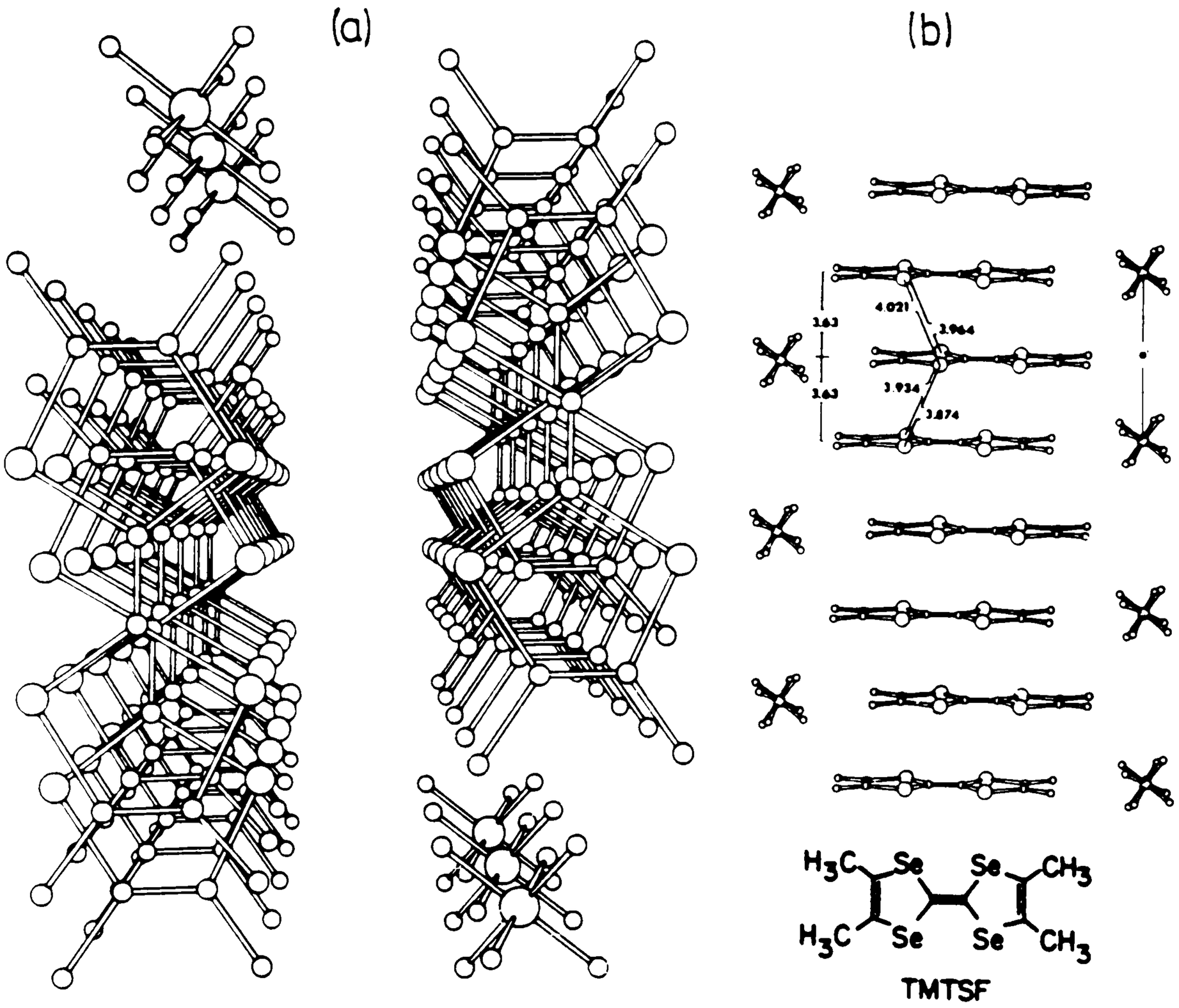


Figure 1.6: *Crystal structure of $(TMTSeF)_2BrO_4$, (a) viewed down the stacking direction and (b) showing the zig-zag stacking of the TMTSeF molecules.*

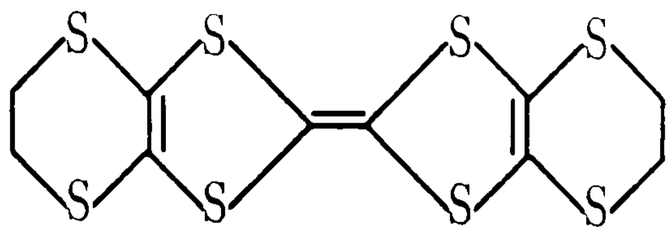
The intermolecular inter- and intra- stack Se··Se distances are all similar (d < 4.00Å), giving rise to an infinite two-dimensional (2-D) sheet of Se··Se interactions. These sheets are separated by the supporting anions, precluding the formation of a 3-D network. Strong interchain delocalisation through the Se··Se network implies that the conductivity is derived entirely from the homoatomic overlap of the selenium atoms. The anions play a negligible, or at most subsidiary, role in the conduction process, although they do indirectly modify the

electrical properties. The Se··Se distances are anion dependent and vary systematically with anion size. Under an applied pressure, the entire Se··Se network shrinks in a predictable, uniform fashion; when the structural architecture best exemplified by the ambient pressure superconductor $(TMTSeF)_2ClO_4$ is achieved, a superconducting transition is structurally favoured[40,43].

The onset of superconductivity requires highly ordered materials. At room temperature, the anions in the Bechgaard salts are in crystallographic disorder, providing a means for electron scattering and thus opposing the onset of superconductivity. On cooling, an anion-ordering transition occurs, which has been extensively studied by magnetic and crystallographic techniques. Comparison of the anion environment in $(TMTSeF)_2AsF_6$ [44] and $(TMTSeF)_2ClO_4$ [45] shows the distorted AsF_6^- ion exists in an isotropic sea of hydrogen atoms with no short H··F contacts, whereas the tetrahedral ClO_4^- ion "sees" an asymmetric hydrogen environment with numerous short H··O contacts. These tend to pin the anion, giving rise to a sluggish anion ordering transition at 24K. In fast-cooled samples, anion-disorder is "frozen-in" below 24K, resulting in complete loss of superconductivity or a severely depressed T_c.

1.4.2.2 $(BEDT\text{-}TTF)_2X$ Salts

More recently, many salts of the multi-sulphur donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, a.k.a. "ET") (17) have been found to exhibit superconductivity. Like the Bechgaard salts, cation-radical salts of ET are grown electrochemically, and many phases can form simultaneously.



(17)

The discovery in 1982 of metallic conductivity stabilised down to 1.4K in $(ET)_2ClO_4(1,1,2\text{-trichloroethane})_{0.5}$ [46] stimulated considerable research on new anionic derivatives of ET. Pressure-induced superconductivity was first observed in unsolvated $(ET)_2ReO_4$ (T_c = 1.5K, 7 kbar)[47]. A number of salts of the $(ET)_2X$ genre are now known to be superconducting; perhaps not surprisingly, X-ray analysis on a number of these salts shows that they are isostructural. Significantly, however, this class of salts differs from the Bechgaard salts in many ways. The ET cations are decidedly non-planar, with the CH_2 groups protruding out of the molecular plane. There is an apparent lack of columnar stacking, the non-planarity of the molecule preventing close π-π interaction (Figure 1.7a). Instead, the $(ET)_2X$ salts have a structure dominated by short "interstack" S··S interactions, giving rise to an infinite 2-D sheet network. This so-called "corrugated sheet network" (Figure 1.7b), by analogy with the Bechgaard salts, provides the main pathway for electrical conductivity.

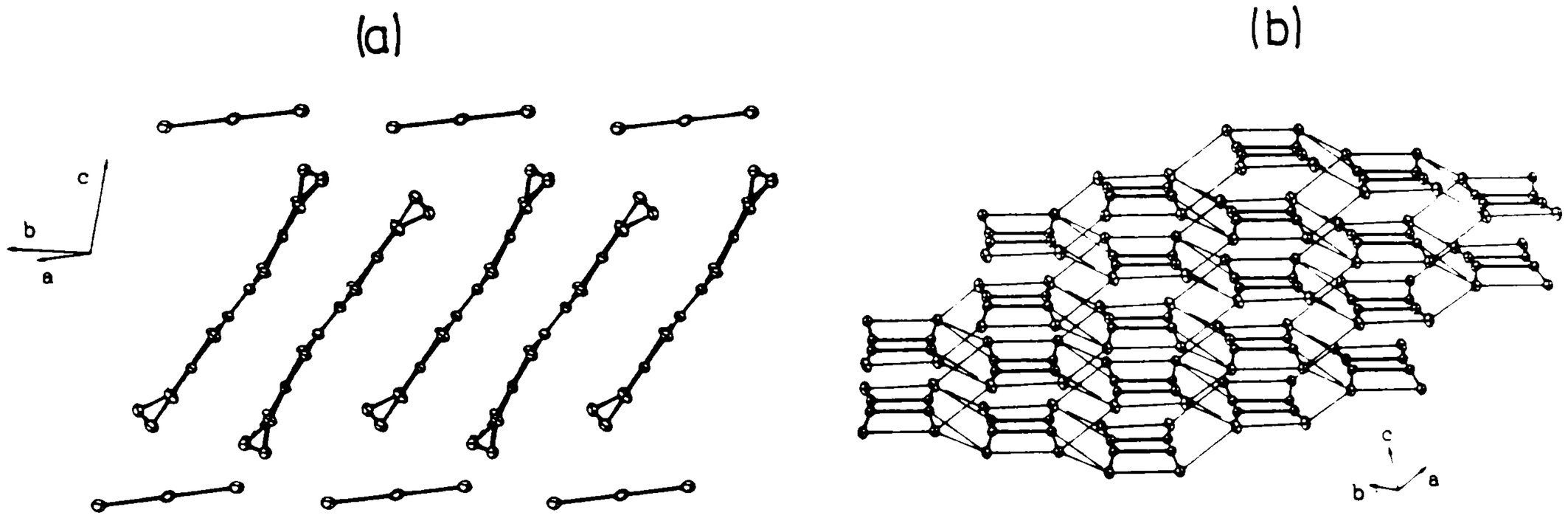


Figure 1.7: *(a) The loose intrastack packing of the ET molecules and I_3^- anions in β-$(ET)_2I_3$ and (b) the two-dimensional "corrugated sheet network" observed in $(ET)_2X$ salts.*

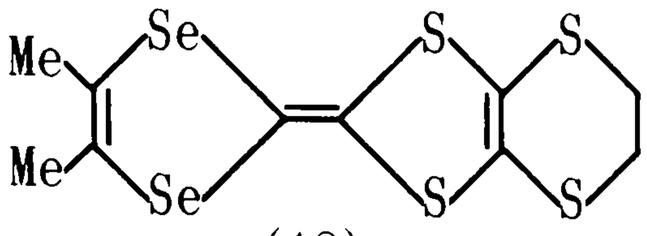
The anions are ordered at room temperature, a pre-requisite for superconductivity, and they reside in the cavities created by the CH_2 hydrogen atoms.

The first example of ambient pressure superconductivity in an $(ET)_2X$ salt was β-$(ET)_2I_3$ (T_c = 1.5K)[49] (the α-phase undergoes an M-I transition at 135K, although tempered α-phases have been reported to be superconducting[50]). The critical temperature may be increased by application of pressure (T_c = 7-8K, 1.3 kbar)[51]. The pressure is believed to prevent a structural modification arising from CH_2 group disorder related to $CH_2 \cdot \cdot I$ interactions. Shorter isostructural anions decrease the "interstack" separations, as predicted, which is accompanied by a rise in ambient pressure T_c [*viz.* β-$(ET)_2I_3$, T_c = 1.5K; β-$(ET)_2IBr_2$, T_c = 2.7K; β-$(ET)_2AuI_2$, T_c = 5K)[52]. Currently, the highest temperature for the onset of superconductivity in an organic compound is 11.2K, observed in the copper thiocyanate salt of ET, d_8-$(ET)_2Cu(SCN)_2$[53], previously reported as 10.4K for the protio sample[54]. While this temperature is considerably lower than those for inorganic ceramics (presently *ca.* 125K), the rate at which the organic T_c has been rising is, nevertheless, impressive: *cf.* $(TMTSeF)_2PF_6$, T_c = 0.9K (12 kbar) in 1980; d_8-$(ET)_2Cu(SCN)_2$, 11.2K (1 bar) in 1988.

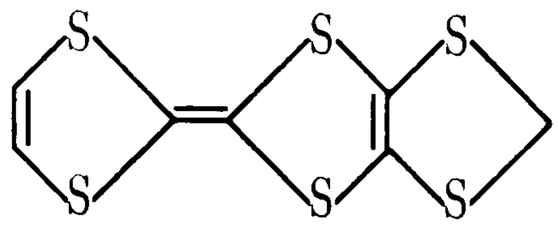
1.4.2.3 $(DMET)_2X$ Salts

The asymmetrical donor dimethyl(ethylenedithio)diselenadithiafulvalene (DMET) (18), formally a hybrid molecule of TMTSeF and ET, also yields superconducting salts. Since the discovery that $(DMET)_2Au(CN)_2$ had T_c = 0.8K at 5 kbar[55], electrochemically grown salts of other linear anions in the $(DMET)_2X$ series have been shown to exhibit superconductivity (X = AuI_2, $AuBr_2$, $Au(CN)_2$, I_3 and IBr_2)[56]. Furthermore, another new

class of superconductor based on an unsymmetrical donor is emerging with the observation of ambient pressure superconductivity in $(MDT\text{-}TTF)_2AuI_2$ (T_c = 3.5K)[57] [MDT-TTF = methylenedithiotetrathiafulvalene (19)].



(18)



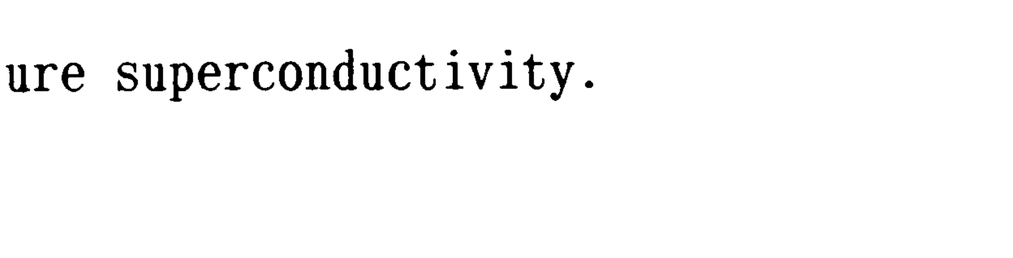
(19)

The $(DMET)_2X$ salts crystallise into three distinct types of structure[56]. One [X = $AuBr_2$] is a sheet structure resembling the $(ET)_2X$ salts; the other two [X = $Au(CN)_2$ and IBr_2] have columnar structures analogous to the $(TMTSeF)_2X$ salts. While the columns are similar in these last two salts, the positions of the anions are very different. However, in all three structural classes, intermolecular S··S contacts are short, giving rise to a high degree of two-dimensionality.

While further studies are in progress, it seems noteworthy that both sheet and columnar packing modes exist in the DMET family, suggesting that the DMET salts may bridge the gap between the $(TMTSeF)_2X$ and $(ET)_2X$ families and provide further insights into the requirements for high temperature superconductivity.

1.4.2.4 $M(DMIT)_2$ Salts

Extensive studies on the sulphur rich 1,2-dithiolene complexes $M(dmit)_2^{n-}$ (20) [based on the the multi-sulphur ligand 4,5-dimercapto-1,3-dithiole-2-thione, (dmit)], have provided the first, and only, examples of superconductivity based on a π-acceptor molecule.



(20) M = Ni, Pd, Pt

Cassoux and co-workers first reported, in 1986, that $TTF[Ni(dmit)_2]_2$ remained metallic to low temperatures, and under an applied pressure became superconducting (T_c = 1.6K, 7 kbar)[58]. There have been subsequent reports of superconductivity in the isomorphous salts $(CH_3)_4N[Ni(dmit)_2]_2$ (T_c = 5K, 7 kbar)[59], α-$TTF[Pd(dmit)_2]_2$ (T_c = 1.7K, 22 kbar)[60] and α'-$TTF[Pd(dmit)_2]_2$ (T_c = 6K, 19 kbar)[60]. X-ray analysis of these salts again shows a high degree of two-dimensionality providing the pathway for superconductivity. The anions are eclipsed, stacking face-to-face in columns; these are connected by many short S··S contacts.

1.4.2.5 Summary

In the search for new organic superconductors, it is imperative to eliminate disorder and to avoid structural modification on cooling, whilst maintaining a 2-D chalcogen atom network. Research is still continuing in earnest on both the "fine-tuning" of anions to optimise these criteria, and the design and synthesis of other new donors. Despite an extensive literature on new organic superconductors, a number of questions still remain, the most prevalent of which is "how high can T_c be raised ?"

1.4.3 TTF Derivatives with Extended π-Systems

The electron donors discussed so far have been limited to those retaining the TTF skeleton, with variations to the periphery. It is clear that if new and exciting solid-state properties are to be achieved, new donors with skeletal structures different from that of TTF must be investigated. Hence, new donors having extended conjugation

between the 1,3-dithiole rings of TTF are currently attracting attention. These donors are expected to fit the numerous criteria already outlined for the design of new donor molecules, having in particular the following desirable features:

(1) More widely spaced sites of maximum spin relative to TTF, which should result in less intramolecular Coulombic repulsion in the doubly ionised state (*cf.* the series TTeF < TSeF < TTF). ESR results have shown the spin population resides mainly on the four sulphur atoms in TTF complexes[61].

(2) The radical cation and dication states should be stabilised by the extended conjugation.

(3) The electron donating ability of these donors should be enhanced, consistent with an extended π-system.

(4) A certain amount of disorder is possible due to rotation about the C-C bonds linking the 1,3-dithiole rings[62].

Since no recent reviews have been published on work in this area, it is worthwhile collating the references here.

The first direction research took in this area was the insertion of aromatic rings between the 1,3-dithiole moieties. Initial targets were those with quinodimethane type skeletons, analogous to those of TCNQ. The preparation of (21) is claimed, without details[63], in an early patent.[1] Further to this, donors (22)-(24) were synthesised, being isolated as their dication salts. All attempts to convert these salts into the neutral donors failed. However, both the diphenyl (22)[64] and dibenzo (23)[65,66] derivatives were observed to form complexes with TCNQ in solution; these could not be isolated in a crystalline form. An

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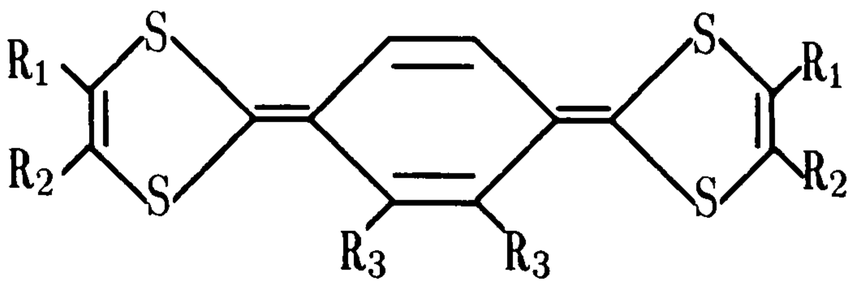
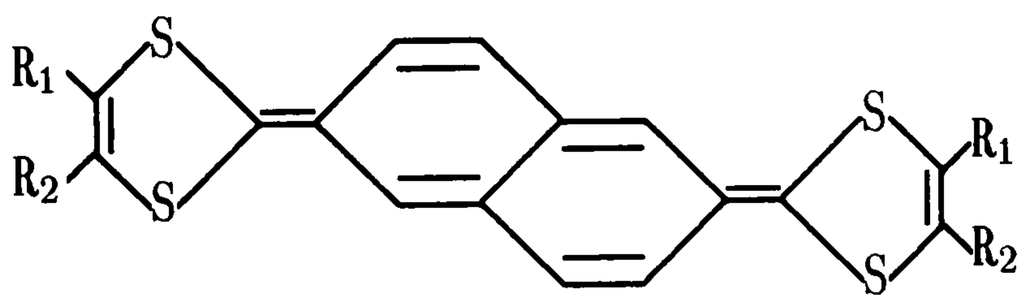
[1] *Note added in proof*: An alternative synthesis of (21) has recently been reported: Y. Yamashita, Y. Kobayashi and T. Miyashi, *Angew.Chem. Int. Ed.Engl.*, 28, 1052 (1989).

iodine complex of (22)[64] and a DDQ complex of (23)[65], have both been reported to be poor conductors (σ_{rt} = 8.5 x 10^{-5} and 3.5 x 10^{-6} S cm^{-1}, respectively). The tetramethyl derivative (24) was found to form a complex with TCNQ and salts with ClO_4^- and BF_4^-, the last two having comparatively high conductivity (σ_{rt} ~ 10 S cm^{-1})[67]. The benzo-fused derivative (25) has been reported, but no complexes are described[68].

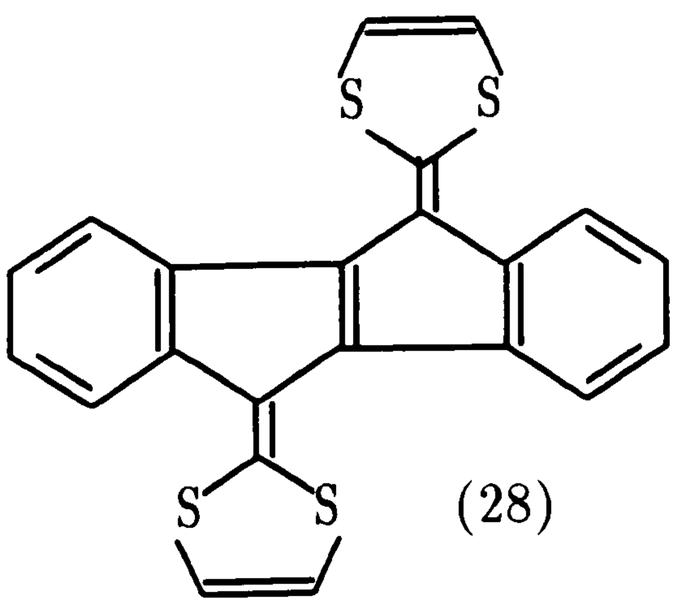


(21) R_1=R_2=R_3=H
(22) R_1=H; R_2=Ph (or isomer); R_3=H
(23) R_1R_2=-(CH=CH)$_2$-; R_3=H
(24) R_1=R_2=Me; R_3=H
(25) R_1R_2=R_3R_3=-(CH=CH)$_2$-

Research into donors with extended conjugation continued with the next target molecules bearing naphthoquinodimethane-related skeletons. Following synthetic precedents set for donors (22) and (24), compounds (26) and (27) were reported as their dication salts: a DDQ complex of (26) and an insulating iodine complex of (27) were discussed[69]. Further donors in this class include compounds (28)[70], (29)[71,72] and (30)[71]; the last two are non-planar, bearing out-of-plane bridging CH_2 groups, and only one complex has been reported, *viz.* an insulating DDQ complex of (29), σ_{rt} = 2 x 10^{-7} S cm^{-1} [71a].



(26) R_1=R_2=Me
(27) R_1=H; R_2=Ph (or isomer)



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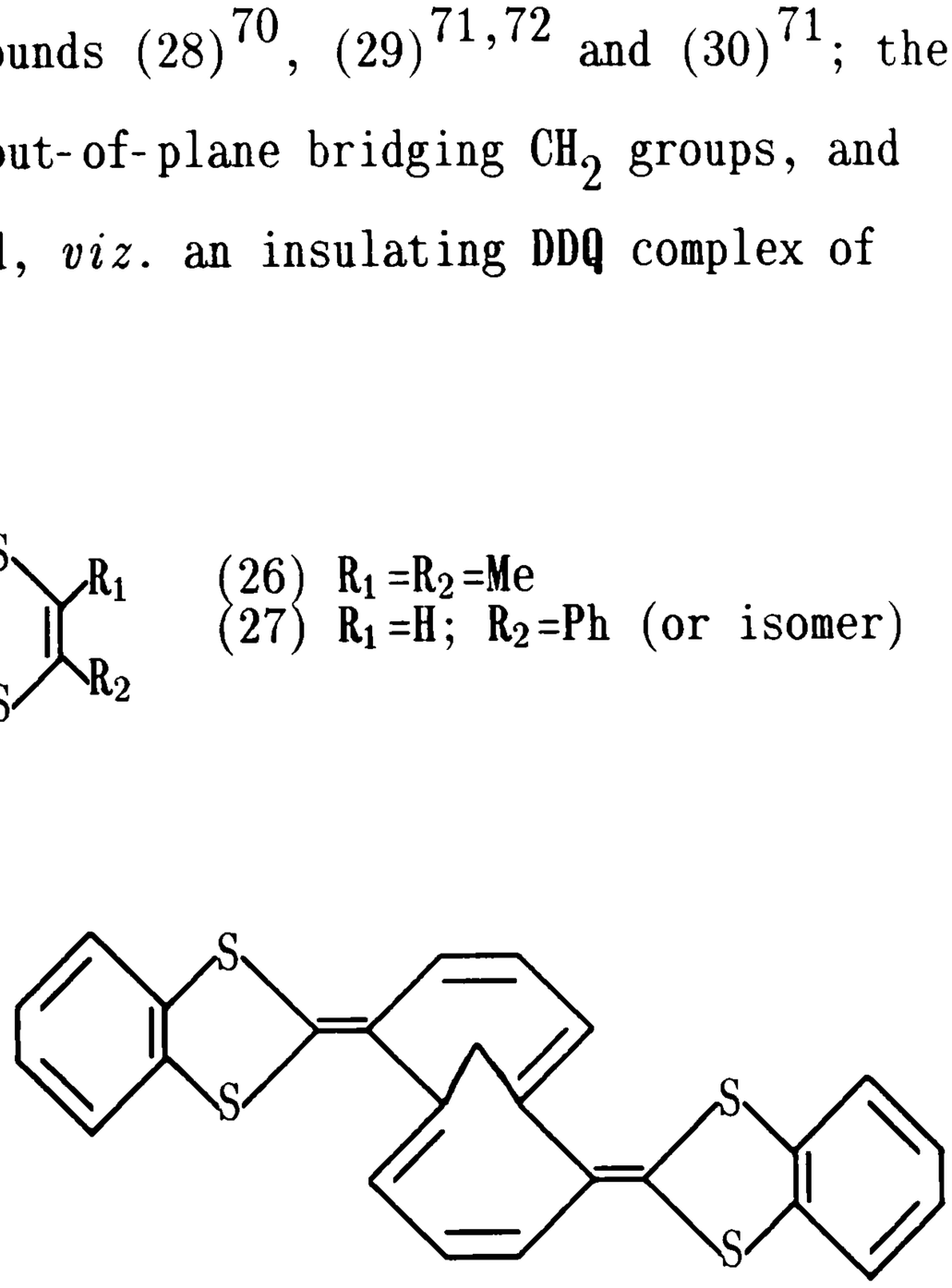

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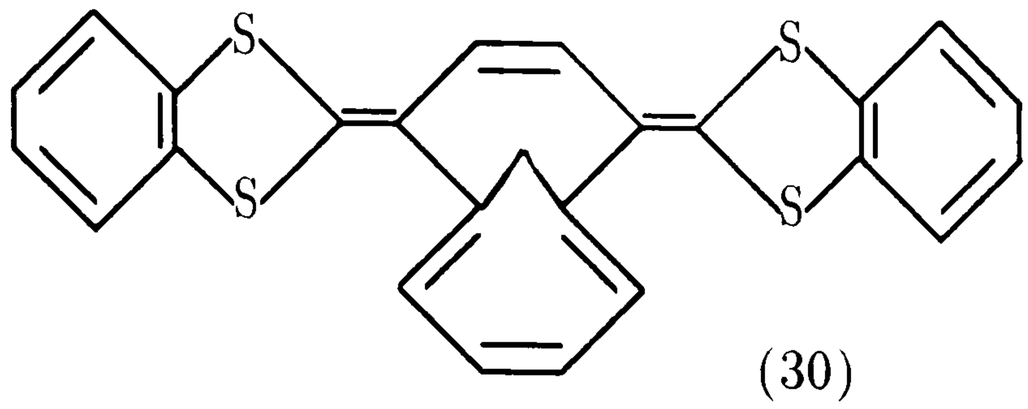
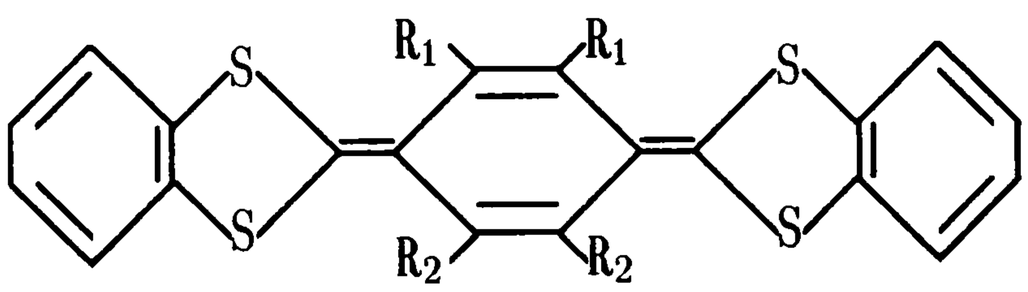
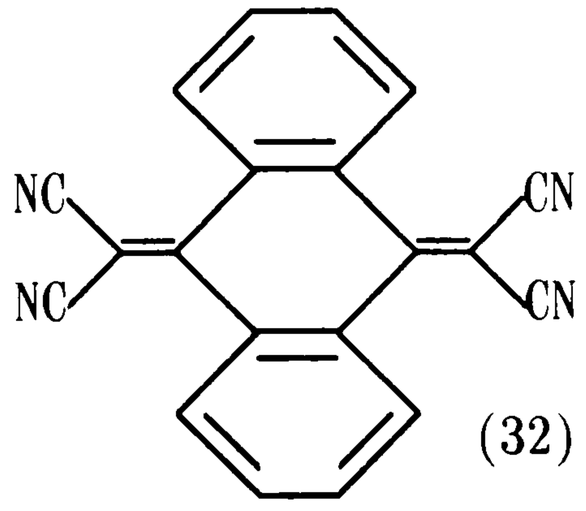


(30)

Further to this, donor (31) was synthesised[73]. By analogy to tetracyano-9,10-anthraquinodimethane (TCNAQ) (32)[74], donor (31) is expected to be non-planar due to steric interactions caused by the peri-hydrogens. This may, in part, explain why the iodine and DDQ complexes of (31) are insulating (σ_{rt} < 1 x 10^{-8} S cm^{-1})[73]. The possibility that this interaction could be removed[75] led to replacement of the benzene rings with thiadiazole rings, yielding compounds (33) and (34)[73]. Iodine and DDQ complexes of donor (33) are semiconducting (σ_{rt} = 10^{-1} - 10^{-3} S cm^{-1}), reflecting a higher degree of planarity in the donor when compared with (31)[73].



(31) $R_1R_1 = R_2R_2 = -(CH=CH)_2-$
(33) $R_1R_1 = -(CH=CH)_2-$; $R_2R_2 = -N=S=N-$
(34) $R_1R_1 = R_2R_2 = -N=S=N-$



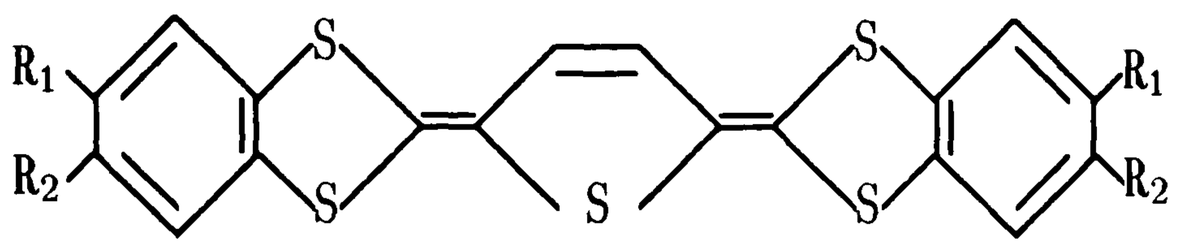
(32)

Cyclic voltammetry on a number of the above donors has been reported (Table 1.3); all show reversible two-electron oxidation waves (the first and second oxidations occur simultaneously). This is a clear indication that on-site Coulombic repulsion has been decreased in the dication, as compared with the TTF dication.

DONOR:	(23)	(25)	(28)	(29)	(31)
$E^{1/2}$ (V)[a]	0.27[b]	0.27[b]	0.32[b]	0.42[c]	0.39[c]

Table 1.3: *Redox potentials of several quinonoid extended donors: (a) 1 x 10^{-4} M donor, 0.1M $[Et_4N][ClO_4]$ in CH_3CN: (b) vs Ag/AgCl (c) vs SCE.*

Finally in this section, recent work has incorporated thienoquinoid extension with a view to increasing the intermolecular interstack bonding through the S··S contact associated with the central chalcogen atom[76]. TCNQ and DDQ have been reported to form stable complexes with donors (35)-(37) with conductivities σ_{rt} = 1 x 10^{-1} to 1 x 10^{-3} S cm^{-1}.

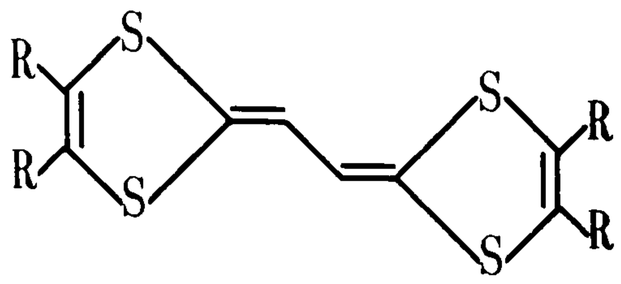


(35) $R_1=R_2=H$
(36) $R_1=H$; $R_2=Me$ (or isomer)
(37) $R_1=R_2=Me$

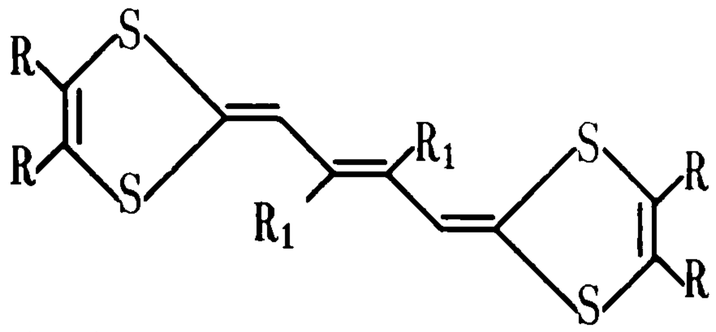
In contrast to data in Table 1.3, the cyclic voltammetric data for compounds (35)-(37) show two well-defined reversible one-electron oxidations, corresponding to the formation of the radical cation and dication[76]. The difference between these two oxidation potentials ($\Delta E = E_2^{ox} - E_1^{ox}$) is, however, significantly less (typically ΔE = 0.25V) than that observed for either TTF (2) (ΔE = 0.35V) or DBTTF (5) (ΔE = 0.35V), again a clear indication that the dication is stabilised as a result of decreased Coulombic repulsion.

Yoshida and co-workers have also pursued new donors with extended conjugation, notably those with sp^2 carbon atoms between the 1,3-dithiole moieties[77]. Thus, compounds (38)[78], (39)[78], (40)[69,78], (41)[79], (42)[79] and (43)[80] were prepared. TCNQ complexes of all of these donors

have been obtained, all of which have 1:1 stoichiometries with σ_{rt} = 10 to 1 x 10^{-2} S cm^{-1} (Table 1.4). Single crystals of (38) show metallic behaviour to 200K, σ_{max} ~ 25 S cm^{-1}.

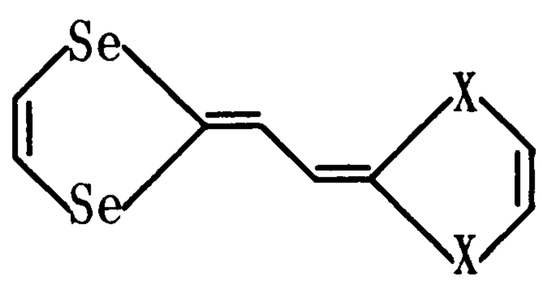


(38) R=H
(39) R=Me
(40) RR=-(CH=CH)$_2$-

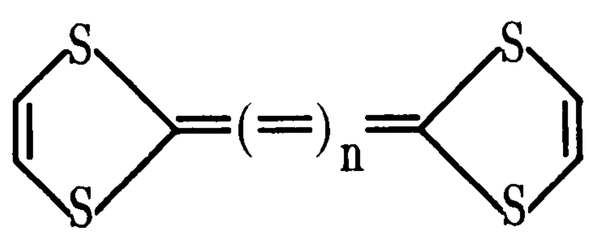


(41) R=H; R_1=H
(42) RR=-(CH=CH)$_2$-; R_1=H
(43) R=H; R_1R_1=-(CH=CH)$_2$-

An extension to this work has seen the replacement of sulphur by selenium to yield the diselena- and tetraselena- derivatives of (38), (44) and (45), respectively[81]. Both form TCNQ complexes of 2:3 stoichiometry (σ_{rt} = 0.2 and 0.1 S cm^{-1}, respectively). Single crystals of TCNQ complexes of donors (38)-(45) have proved difficult to grow - this has been attributed to a lack of tight intermolecular stacking due to the presence of a flexible C-C bond. Research was extended to synthesise the rigid donors (46) and (47), having two and four cumulenic carbon atoms inserted between the 1,3-dithiole rings. Donors (46) and (47) could not be isolated due to their extreme instability, but have been characterised as their dication salts[82].



(44) X=S
(45) X=Se



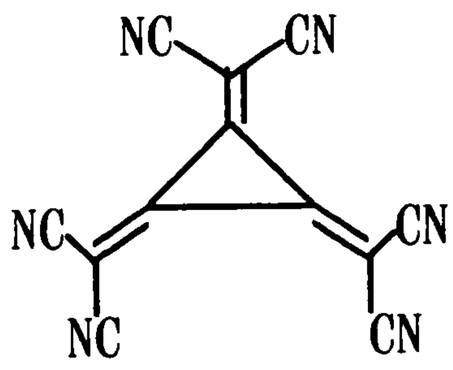
(46) n=1
(47) n=3

Cyclic voltammetric data for donors (38)-(45) are summarised in Table 1.4[77], and again clearly indicate that Coulombic repulsion in the dications is decreased. In terms of donor ability, all are better donors than TTF (*ie.* E_1 values are lower than for TTF).

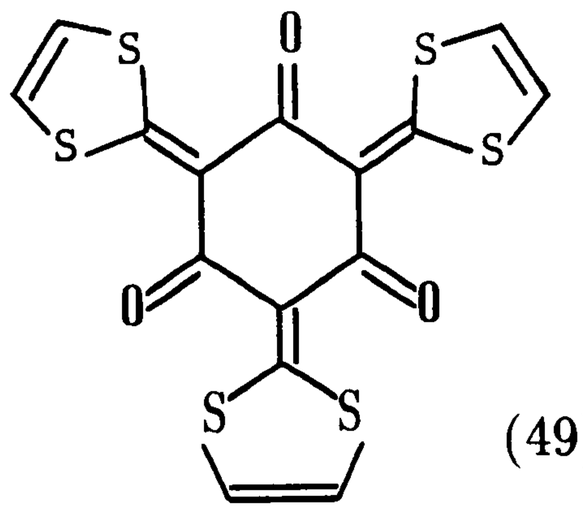
DONOR	REDOX POTENTIALS[a] E_1	E_2	D:A	σ(rt)[b] S cm^{-1}
(38)	0.20	0.36	1:1	0.79
(39)	0.26	0.41	1:1	~ 5
(41)	0.22		1:1	----
(42)	0.47		1:1	----
(43)	0.23		1:1	0.26
(44)	0.26	0.40	2:3	0.07
(45)	0.33	0.47	2:3	0.25
TTF	0.34	0.71	1:1	500

Table 1.4: *Redox potentials and conductivities of TCNQ salts of vinylogues of TTF; (a) 1 x 10^{-4} M donor, 0.1M $[Et_4N][ClO_4]$ in CH_3CN, vs Ag/AgCl; (b) compressed pellet, four-probe measurement.*

A final area worthy of brief mention here, is that of donors which possess a higher degree of symmetry than the traditional pseudo two-fold symmetry of TTF derivatives. Several years ago Fukunaga synthesised a TCNQ-inspired molecule (48) with D_{3h} symmetry[83], and Watson reported compound (49)[84].

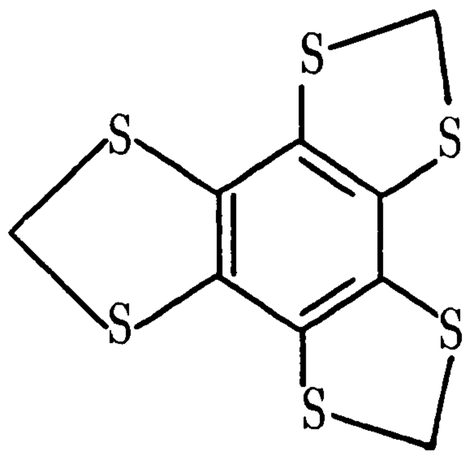


(48)



(49)

This direction of research has been stimulated by recent theories that organic ferromagnetism may exist in salts of donors having odd-fold symmetry[85]. Guided by theory, several groups have studied complexes and cation-radical salts of organic donors with C_3 symmetry, eg. (50), (51) and (52)[86].



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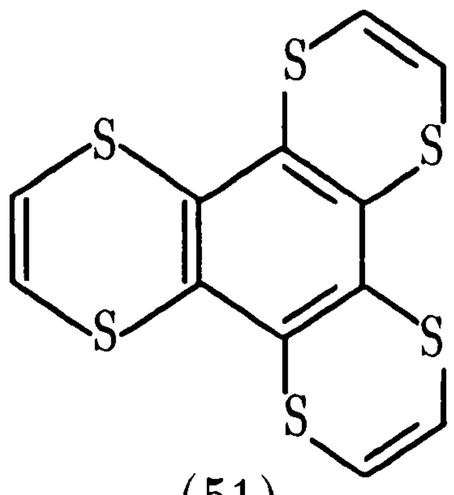

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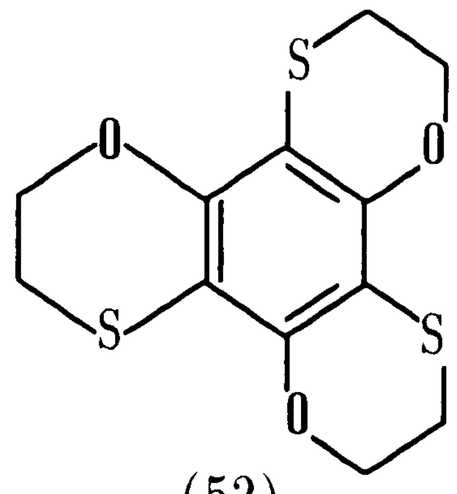
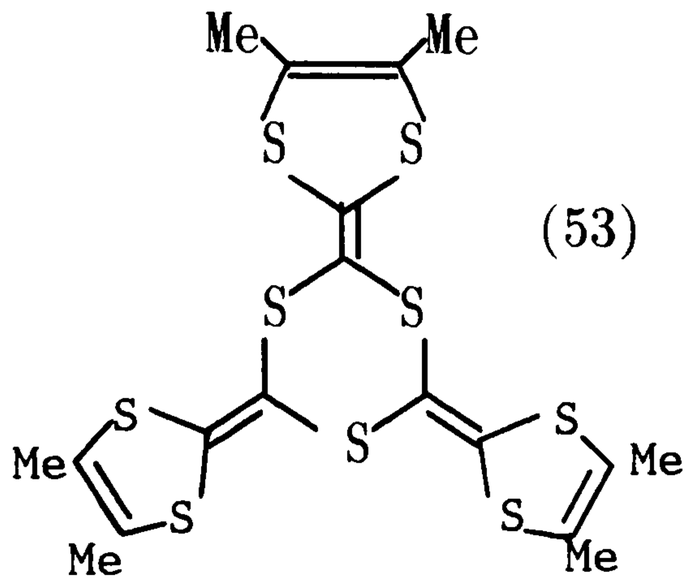
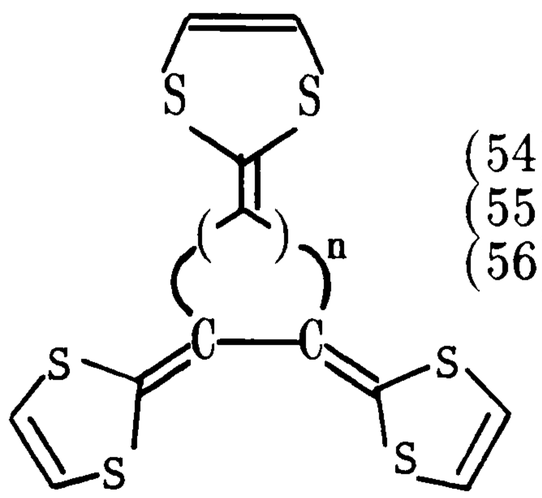


(52)

Recently, Cava and Yoshida have independently prepared cyclic donors based on the 1,3-dithiole ring possessing high degrees of symmetry *viz.* donors (53)[87], (54)[88], (55)[89] and (56)[90]. In all cases, the severe non-planarity of the donors has precluded complex formation.



(53)



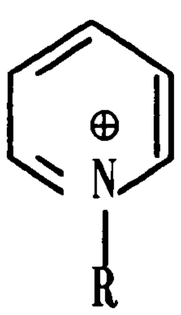
(54) n=2
(55) n=3
(56) n=4

1.4.4 Electroactive Langmuir-Blodgett Films

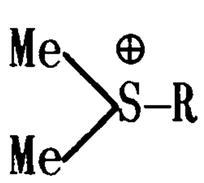
The solid-state properties observed in C-T complexes are critically dependent upon inter- and intra-molecular interactions. Most conducting complexes have been characterised as single crystals or microcrystalline powders. However, a promising new direction for research on C-T complexes is emerging with recent reports of electroactive Langmuir-Blodgett (LB) films. The well known LB technique enables the transfer of a monomolecular layer from a water surface to a solid substrate in an organised, close-packed fashion to yield ultra-thin films of controlled thickness and regular molecular arrangement[91]. The molecules employed in the LB technique are designed to have a hydrophilic group attached to

one, or several, hydrophobic long aliphatic chains (typically > C_{16}). The LB method is by essence different from the classical crystal growth techniques, the film being built up one layer after another. Close ordered face-to-face stacking of molecules is enforced by the method of film deposition and intermolecular side-chain interactions.

The initial reports that C-T complexes could form electroactive LB films were from Barraud and co-workers in 1985[92]. As deposited, LB films of the 1:1 complex N-docosylpyridinium [NDP,(57)]-TCNQ exhibited low lateral conductivity (σ_{rt} = 1 x 10^{-5} to 1 x 10^{-6} S cm^{-1}). However, on doping with iodine vapour, films of conductivity σ_{rt} ~ 1 x 10^{-1} S cm^{-1} were obtained. Similar behaviour was observed for the film of dimethyloctadecylsulphonium (58)-TCNQ[93].



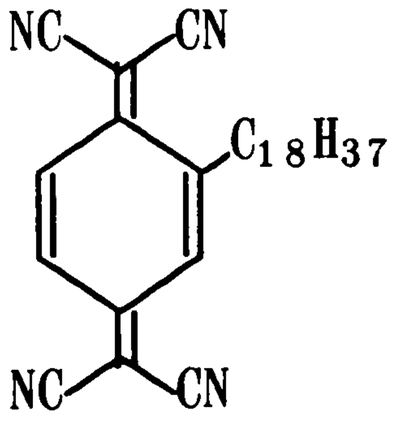
(57) R=$C_{22}H_{43}$
(59) R=$C_{18}H_{37}$



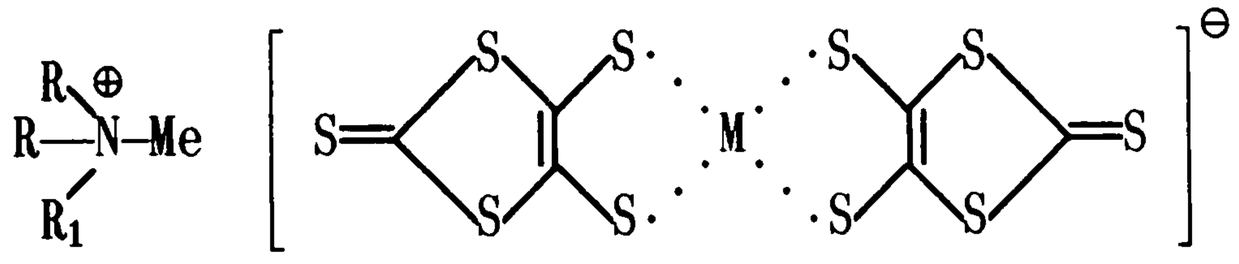
(58) R=$C_{18}H_{37}$

In both cases, the crystalline complexes are insulating as a result of complete charge-transfer (hence, a filled conduction band). Doping of a classical crystalline C-T complex is impossible as the dopant cannot enter the crystal. On the contrary, small molecules (*eg.* I_2) may diffuse into an LB film. The result in the above examples, is competition between I_2 and TCNQ to accept an electron from the donor, yielding a partially filled conduction band (hence, the observed enhanced conductivity). LB films of the 1:2 complex NDP$(TCNQ)_2$ have an as-deposited conductivity of 1 x 10^{-1} S cm^{-1} [94], consistent with TCNQ being in a non-integral oxidation state. More recent work in our laboratory has shown that multilayers of N-octadecylpyridinium (59)-TCNQ are also conducting without doping[95] - the precise source of the relatively high conductivity remains unclear.

The initial work on multilayers of these cation-TCNQ complexes prompted the study of amphiphilic acceptors; LB films based on alkyl-substituted TCNQ, with TTF and TMTTF, have been quite extensively studied. For example, a multilayer film of TMTTF-octadecylTCNQ (60) is conducting without doping[96], consistent with a partially filled conduction band. The film exhibits highly anisotropic conductivity, typical of electroactive LB films; the conductivity in the lateral direction is 1×10^{13} times greater than that in the normal direction. This is well explained by the lamellar structure of the film, in which the close stacking of the conducting plane yields segregated columns separated by the insulating long alkyl chains. With the report of superconductivity observed in crystalline $Me_4N[Ni(dmit)_2]_2$, a study of LB films of alkylammonium-$Ni(dmit)_2$ salts has been undertaken by Nakamura *et al.*[97] The mixed films of (61) with icosanoic acid show conductivities of $\sigma_{rt} = 1 \times 10^{-1}$ to 1×10^{-3} S cm^{-1} after bromine oxidation[97], and a mixed-film of (62) has a reported conductivity of σ_{rt} = 25 S cm^{-1} after doping[98].



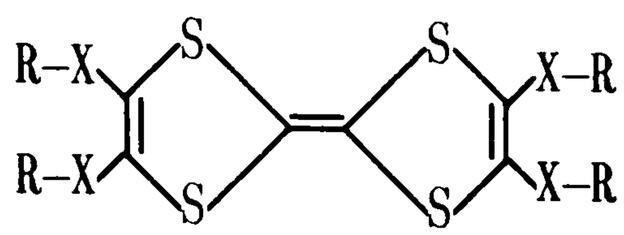
(60)



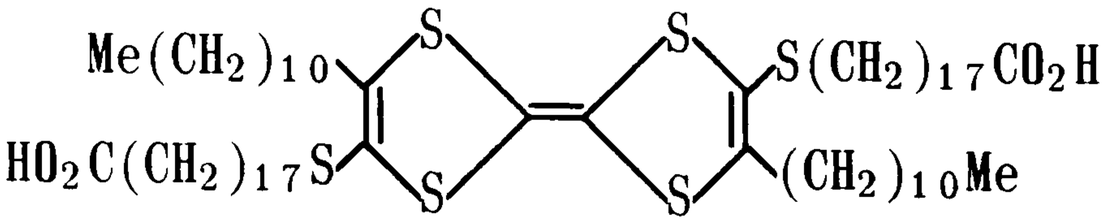
(61) R_1 = Me; R = C_nH_{2n+1} (n = 10-20); M = Ni, Au
(62) R = R_1 = $C_{10}H_{21}$; M = Au

The most recent direction research has taken is the study of amphiphilic donors. The first hydrophobic TTF derivatives were described by Saito[99]. These derivatives (63) have been studied as single crystals, but have not been reported to form LB films. Robert and co-workers have described poor quality films of (64)[100], and a synthetic methodology to TTF derivatives bearing two (65) and four (66) alkyl chains attached

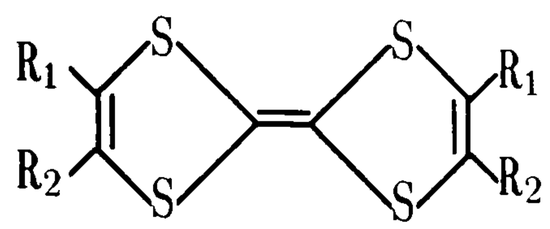
through carbon has been established in our laboratory[101]; LB films of these materials have, however, not been obtained.



(63) $R=C_nH_{2n+1}$ (n=1-18); X=S or Se

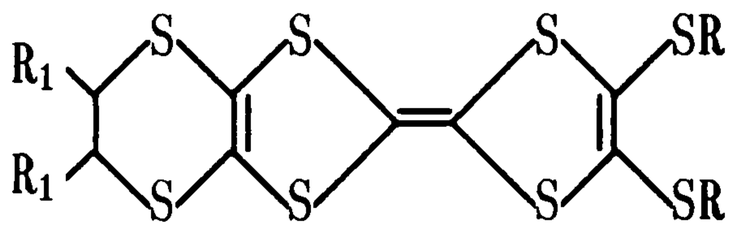


(64)

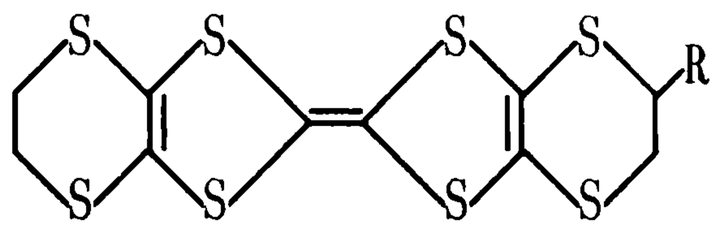


(65) $R_1=R_2=C_5H_{11}$
(66) $R_1=H$; $R_2=C_{18}H_{37}$ (or isomer)

A number of groups are presently investigating multilayers of ET derivatives bearing two thioalkyl chains. For example, donors (67) and (68) form arachidic acid (5-50%) stabilised films which are insulating, even after doping[102]. The completely ionic $TCNQF_4$ salts of (67) and (68), however, form good films of conductivity σ_{rt} = 1 x 10^{-1} to 1 x 10^{-2} S cm^{-1} after doping with iodine[102].



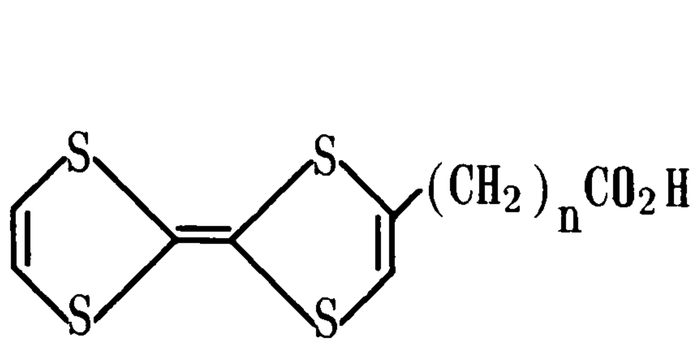
(67) $R_1=H$; $R=C_nH_{2n+1}$ (n=12,16,18)
(68) $R_1=Me$; $R=C_{16}H_{33}$



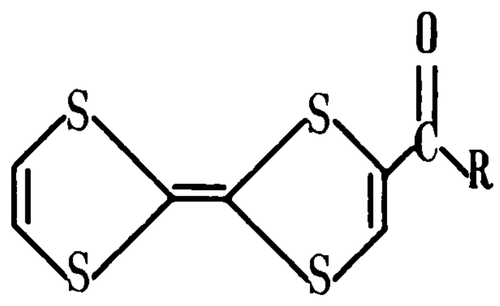
(69) $R=C_nH_{2n+1}$ (n=16,18,20)

Attention has also been focused on TTF derivatives bearing one alkyl chain. The ET derivatives (69) have been shown to form fatty acid stabilised films (50% stearic acid) which are insulating on doping[103]. Bechgaard *et al.* have studied TTF substituted with fatty acids (70) in an attempt to stabilise the as-deposited film intramolecularly; however, it seems that these molecules do not yield good quality LB films[104]. In contrast, work in our laboratory has concentrated on alkanoyl-TTF derivatives (71) which, in contrast to all the previous TTF derivatives

discussed, form exceptionally high quality films without fatty acid stabilisation. For example, multilayers of hexadecanoyl-TTF (71a) are stable, with conductivity σ_{rt} = 1 x 10^{-5} S cm^{-1} increasing to σ_{rt} = 1 x 10^{-2} S cm^{-1} after iodine doping[105].



(70) n=10-15



(71) $R=C_nH_{2n+1}$
(71a) n=15
(71b) n=17

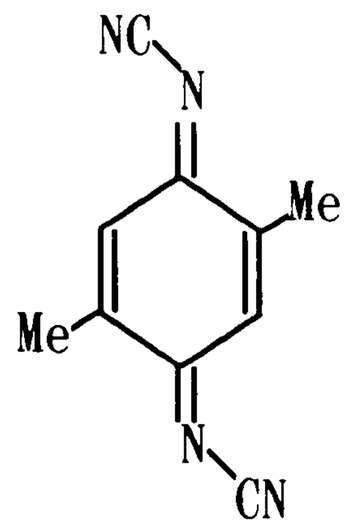
1.5 NEW ELECTRON ACCEPTORS

Although there have been some significant developments with new electron acceptors, there has been far less work published in this area compared with new donors. A major reason for this lies in the difficulty of synthesis of suitable acceptors. A comprehensive discussion is beyond the scope of this thesis, and the reader is referred to a recent review[106].

Extensive research into new acceptors based on the TCNQ skeleton has resulted in the conclusion that, in general, substitution or extension of the basic TCNQ skeleton leads to complexes that are less conducting than TTF-TCNQ itself.

Possibly the most exciting development in work on new acceptors is due to Hünig and co-workers, who replaced the dicyanomethylene groups [=$C(CN)_2$] of TCNQ with N-cyanoimine groups (=N-CN)[107]. The result has been the exceptionally high conductivity observed in the copper salt of 2,5-dimethyl-N,N'-dicyanoquinonediimine (2,5-DMDCNQI) (72). This salt has σ_{rt} ~ 800 S cm^{-1}, rising to 5 x 10^5 S cm^{-1} at 3.5K[108]. A range of 2,5-disubstituted N,N'-dicyanoquinonediimines with various metal ions

have since been studied, and may in time provide a new class of organic superconductor.



(72)

In summary, research over the last twenty years has failed to establish a class of molecules which is far superior to TCNQ. Consequently, our knowledge of the role of the acceptor in determining solid-state properties is still rather limited, leaving considerable scope for new research.

1.6 APPLICATIONS

Undoubtedly, a major impetus behind much of this research has stemmed from the potential technological applications in the electronics industry. The key advantages of the organics over traditional inorganic materials are their extremely small size, structural diversity and potential low cost. Despite this, the practical applications are still largely exploratory, and their inroads into commercial uses are limited. This may be partly because of the frailty of the organic crystals as compared with the industrially more acceptable and processible conducting polymers. Present day applications include photochemical switches, components of solar cells and lithographic resist materials. The recent advances in LB films of C-T complexes offers new possibilities in device technology, removing the necessity for growing and handling frail single crystals. Possible uses are in molecular rectifiers and pyroelectric sensors.

Continued research in the field of organic metals will inevitably lead to a far greater understanding of quasi 1-D conductivity, and may, in turn, provide an insight into the necessary criteria for the design of a room temperature superconductor. It is this possibility which makes the continued study of organic metals both exciting and essential.

CHAPTER TWO

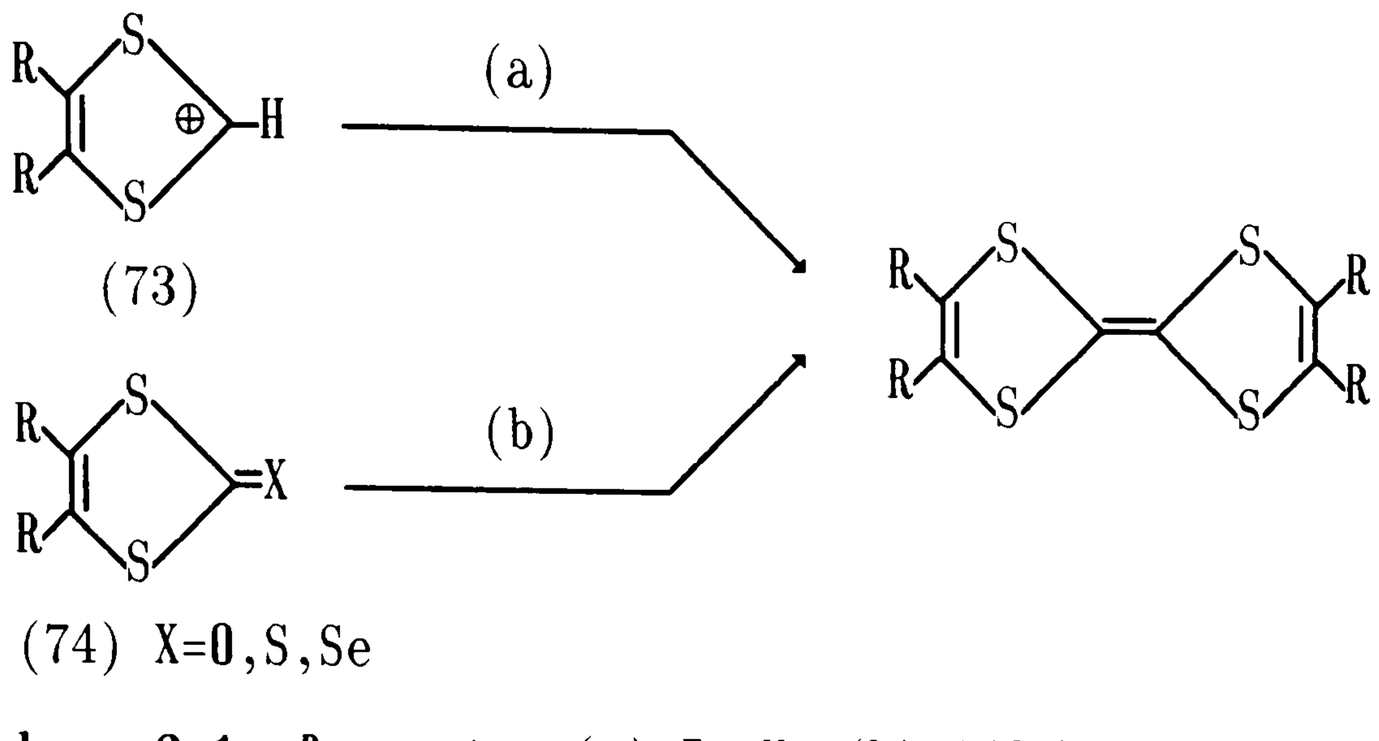
HIGHLY CONJUGATED BIS(1,3-DITHIOLE) DERIVATIVES

2.1 INTRODUCTION

In the search for new molecular metals, electron donors that are substituted derivatives of the parent TTF, and its chalcogen analogues, continue to command attention. An important concept in stabilising the metallic state is the reduction of on-site Coulombic repulsion in charged species. It has been argued that unless one of the components of a C-T complex can support a doubly charged species, then only a correlated type of conductivity is possible[31a]. This theory has contributed to the current interest in derivatives of tetratellurafulvalene (TTeF), for which the greater polarisability of the tellurium, relative to selenium and sulphur, has been shown to reduce Coulombic repulsion in the dication state (Chapter 1.4.1). An alternative approach to stabilising the dicationic state, that forms the subject of this chapter, is to extend the conjugation between the 1,3-dithiole rings of TTF. A number of donors of this type are known (Chapter 1.4.3). Before discussing our work in this area, it is worthwhile reviewing the synthetic approaches to extended donors.

2.2 SYNTHETIC STRATEGIES TOWARDS EXTENDED BIS(1,3-DITHIOLE) DONORS

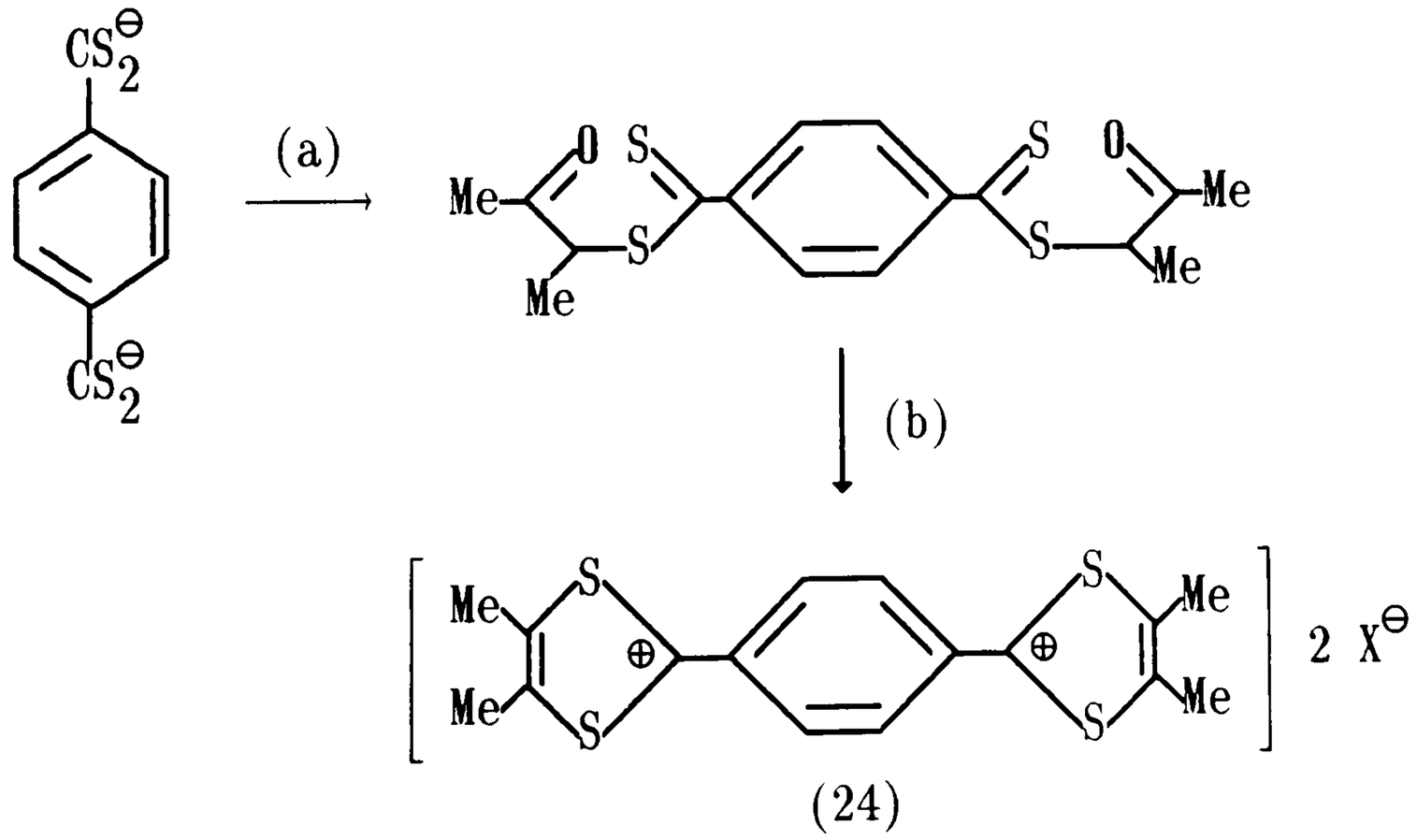
The most widely used routes to TTF derivatives proceed *via* coupling reactions between the C(2) atoms of 1,3-dithiolium salts (73) or 1,3-dithiole-2-ones, -thiones, or -selenones (74) (Scheme 2.1)[20]. Couplings of this type are clearly not applicable to extended donors. Alternative synthetic strategies that are suitable for highly conjugated TTF analogues may be conveniently divided into three classes.



Scheme 2.1: *Reagents: (a) Et_3N; (b) $P(OR')_3$ or PR'_3.*

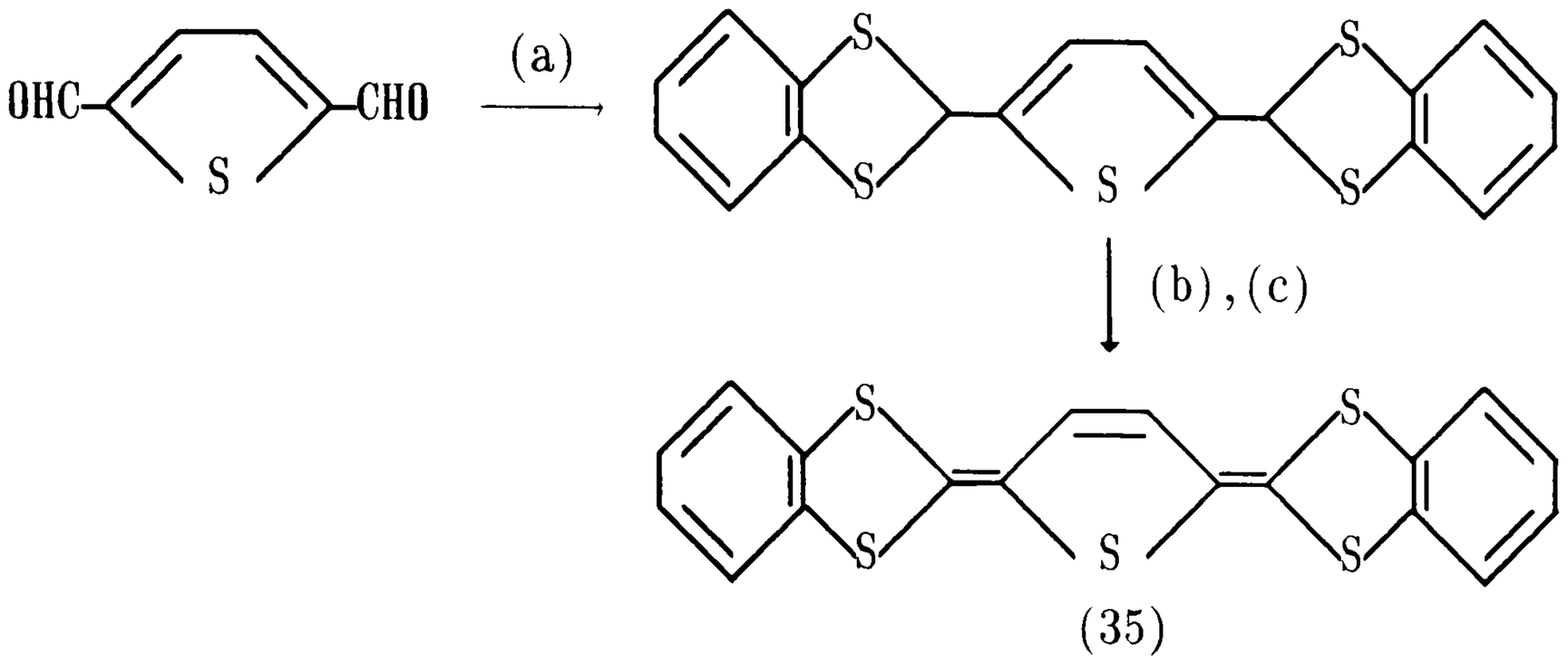
2.2.1 Intramolecular Assembly of the 1,3-Dithiole Rings onto a Difunctionalised Bridging Group.

This synthetic strategy was first employed in the preparations of benzoquinonoid derivatives (22)[64] and (24)[67] and subsequently in the synthesis of naphthoquinonoid donors (26) and (27)[69]. This route is outlined in Scheme 2.2 for compound (24); the 1,3-dithiole ring is assembled by condensation of a bis(dithiocarboxylic acid) with an appropriate α-haloketone, followed by acid catalysed dehydrative cyclisation. This approach yields the donors as their oxidised dication salts.



Scheme 2.2: *Reagents: (a) $MeC(=O)CHXMe$; (b) conc. H_2SO_4.*

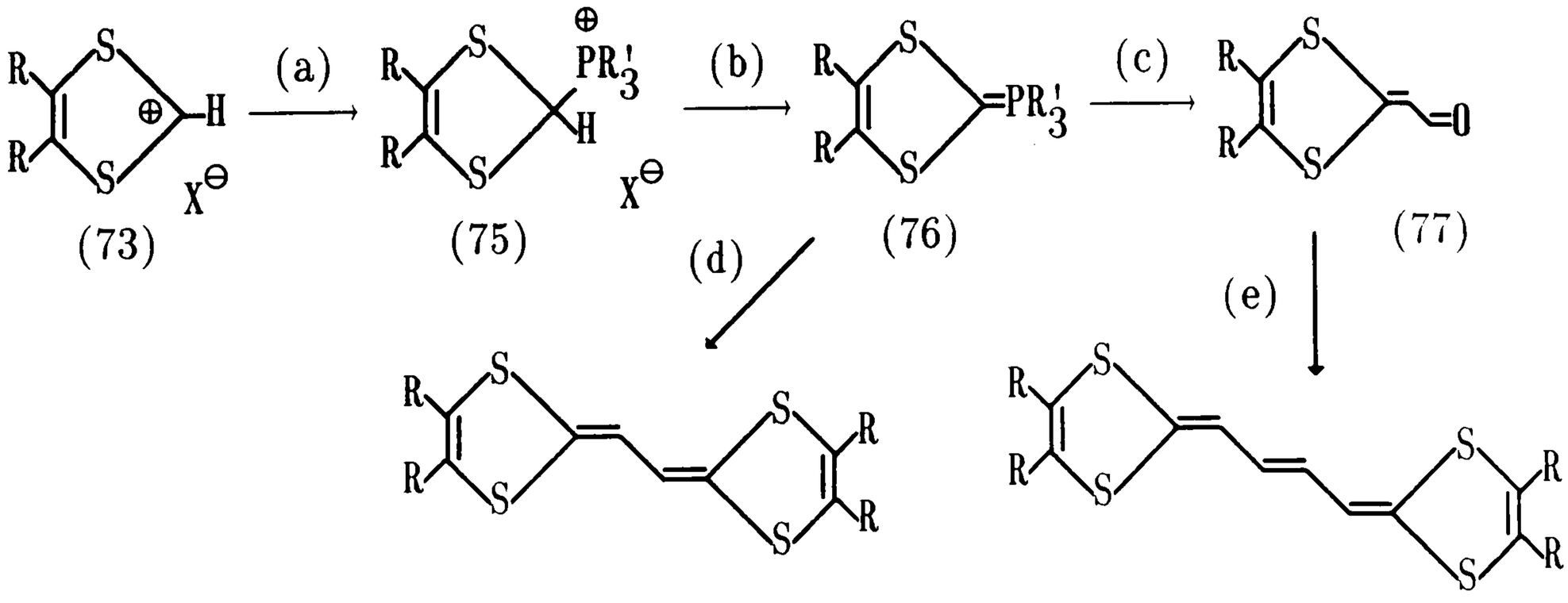
The 1,3-dithiole skeleton has also been constructed by condensation of a 1,2-dithiol (invariably benzene-1,2-dithiol) with a dialdehyde: subsequent hydride abstraction, followed by deprotonation, can yield the neutral donor[65,68,69,76]. This route is exemplified in Scheme 2.3[76].



Scheme 2.3: *Reagents: (a) $HS-C_6H_4-SH$; (b) $Ph_3C^+SbCl_6^-$; (c) Et_3N.*

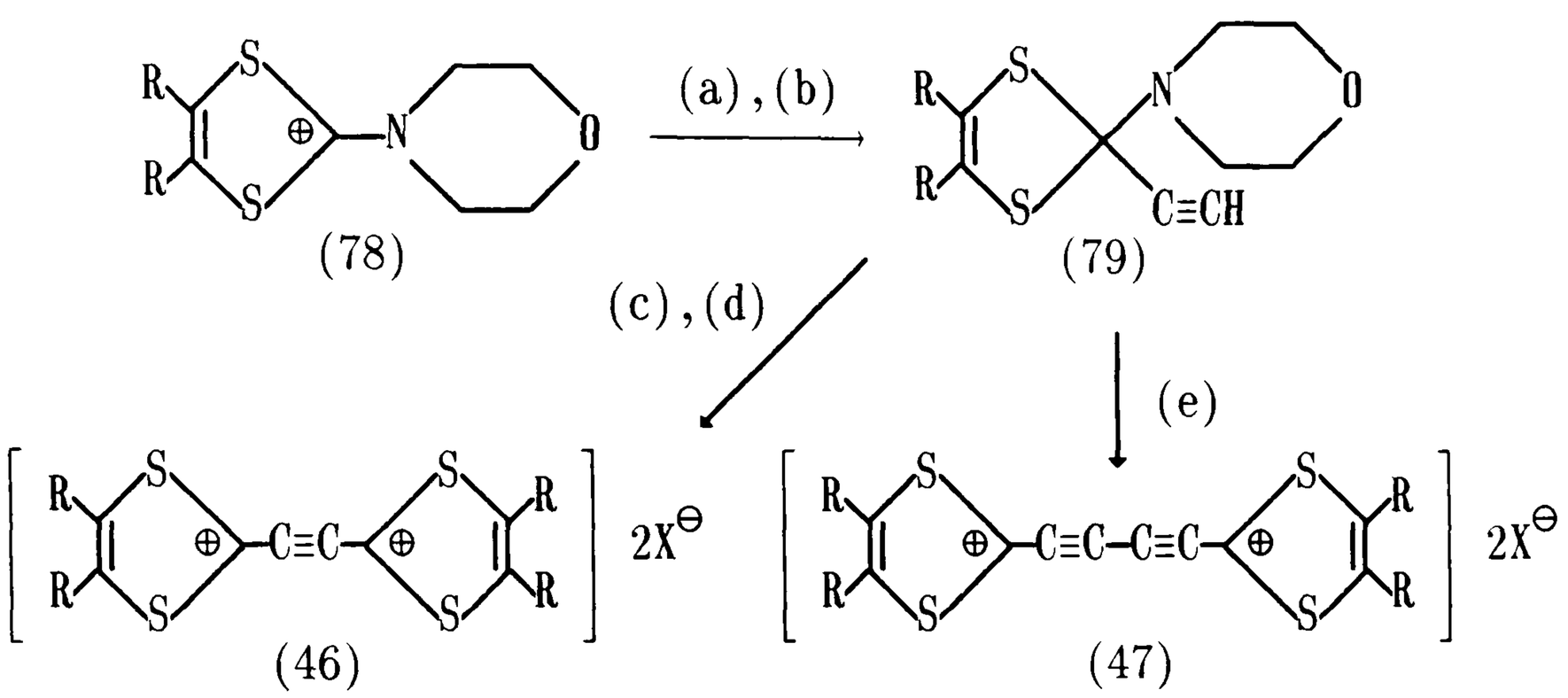
2.2.2 Intermolecular Reaction of 2-Substituted 1,3-Dithioles

1,3-Dithiolium cations (73) react readily with trialkylphosphines to form the corresponding phosphonium salts (75)[109]. The ylids (76), derived from these salts, have been extensively utilised by Yoshida *et al.* in the efficient synthesis of TTF vinylogues (38)-(43) (Scheme 2.4)[78,79].



Scheme 2.4: *Reagents: (a) PR_3'; (b) n-BuLi; (c) OHCCHO; (d) reagent (77); (e) $LiAlH_4/TiCl_3$.*

Reaction of 1,3-dithiolium cation (78) with trimethylsilylethynyl-magnesium bromide followed by desilylation yields acetylenic derivative (79); coupling of (79) with a 1,3-dithiolium cation, or Eglington coupling of (79), yields dications (46) and (47), respectively (Scheme 2.5)[82]. Electrochemical reduction has shown that the neutral cumulenes are extremely unstable.

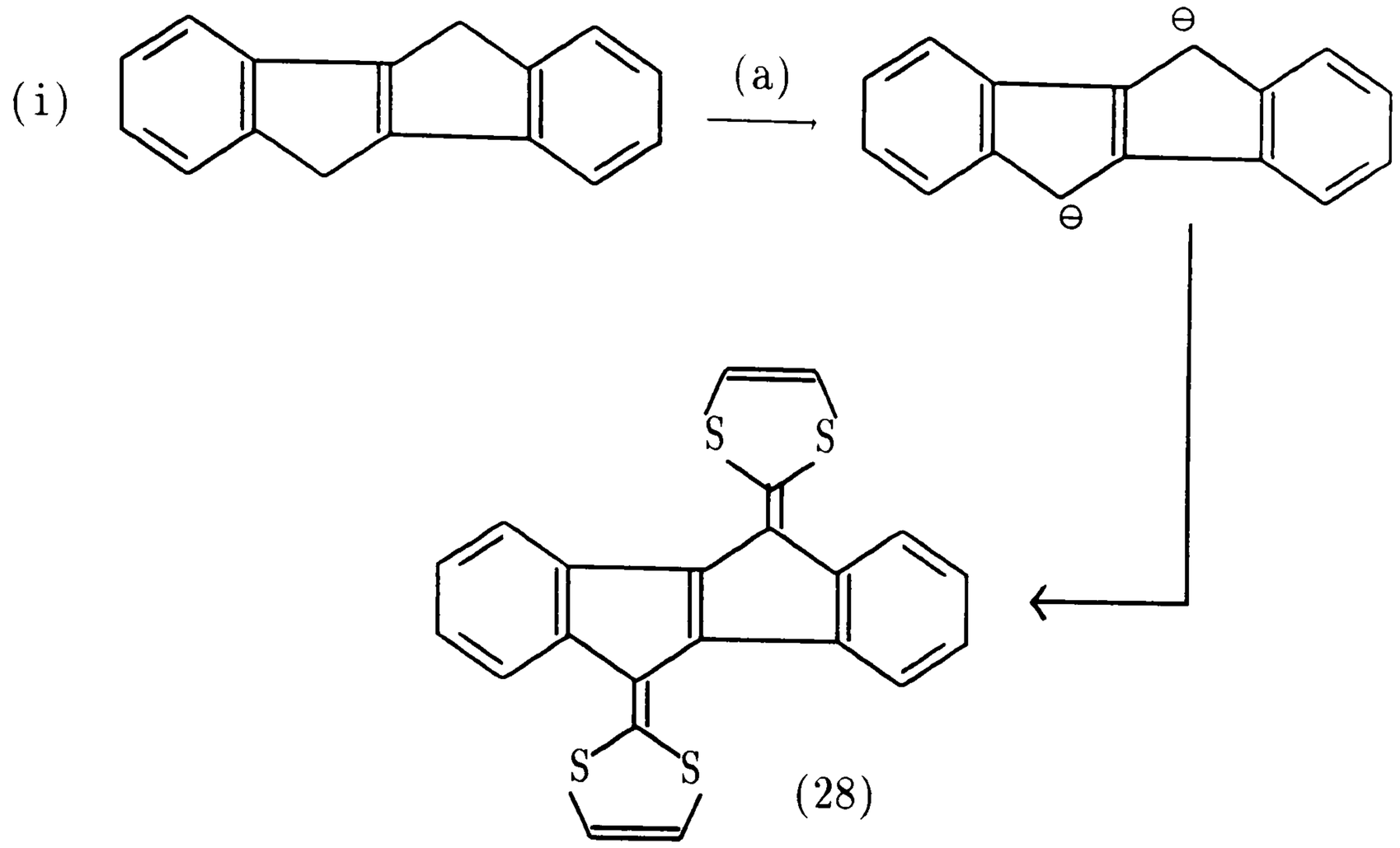


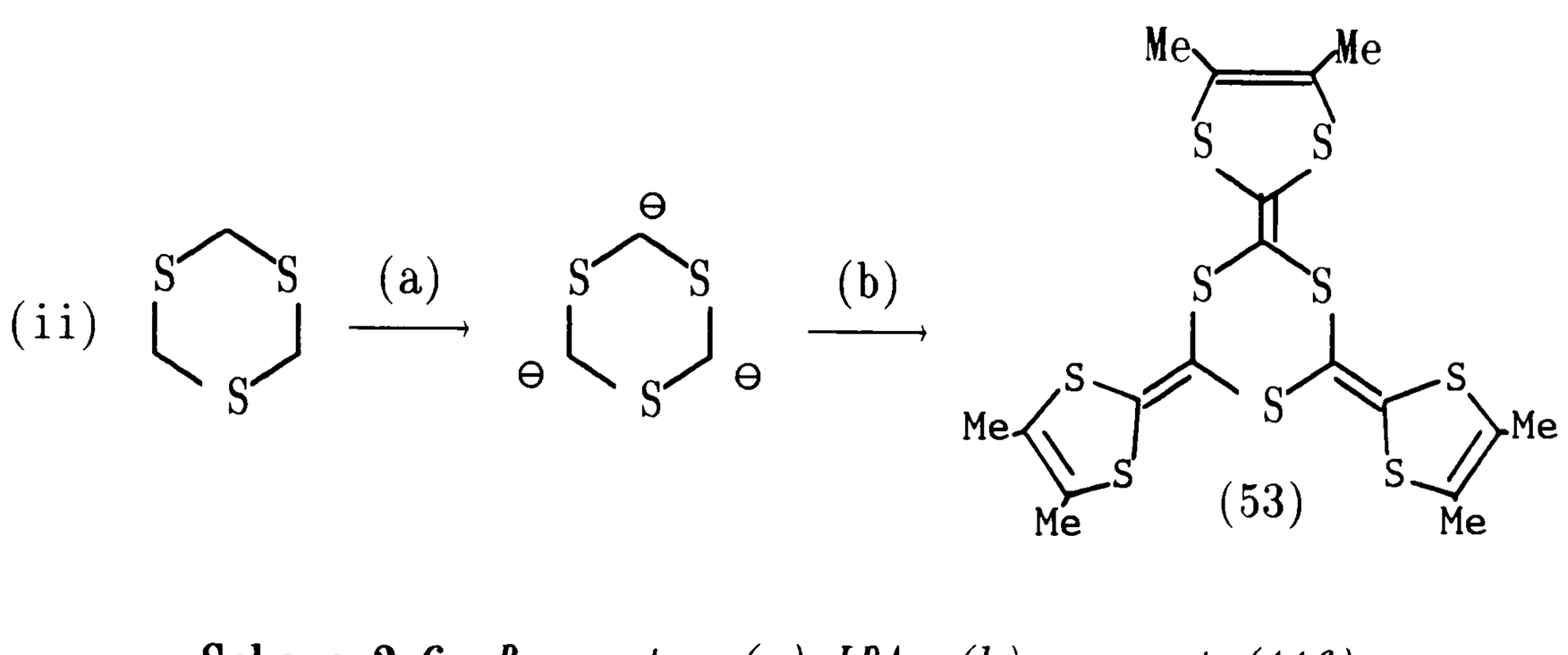
(78) (79) (46) (47)

Scheme 2.5: *Reagents: (a) TMS–C≡CMgBr; (b) n-Bu$_4$N$^+$ F$^-$; (c) LDA; (d) reagent (78); (e) Cu(OAc)$_2$.*

2.2.3 Trapping of the Dianion of the Bridging Group

The condensation reactions of 2-methylthio-1,3-dithiolium salts with cyclopentadienide anions and active methylene groups was investigated in the late 1960's by Gompper *et al.* as a route to 2-alkylidene-1,3-dithioles[110,111]. This methodology has recently received renewed attention as a route to novel extended donors (Scheme 2.6)[70,87].





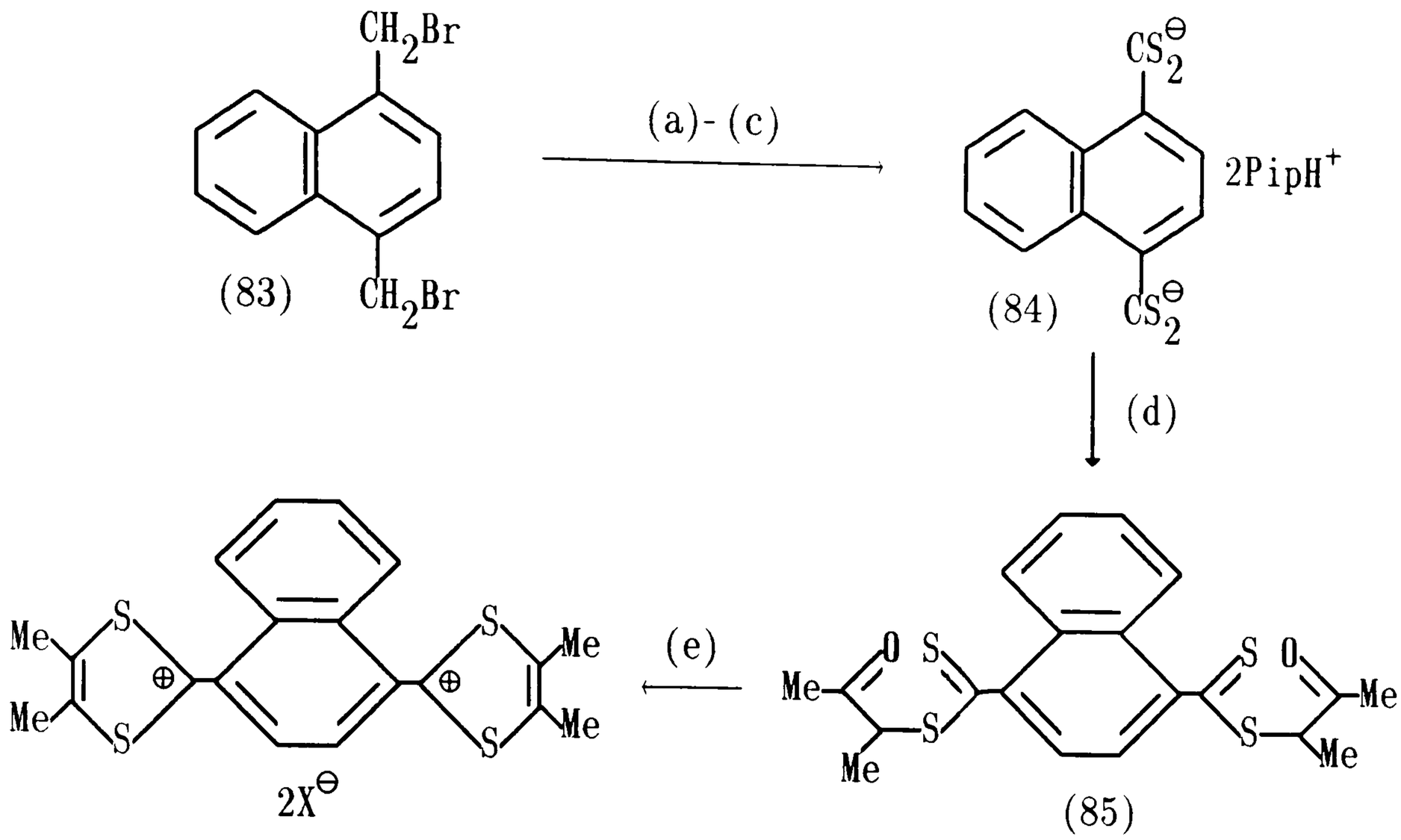
Scheme 2.6: *Reagents: (a) LDA; (b) reagent (116).*

2.3 EXTENDED BIS(1,3-DITHIOLIUM) DICATIONS

2.3.1 Synthesis of Bis(1,3-dithiolum) Dications (80)-(82)

We initially targeted our attentions on three new extended bis-(1,3-dithiolium) dications, namely 1,4-naphthalene-bis(4,5-dimethyl-1,3-dithiolium) (80)[112,113], 9,10-anthracene-bis(4,5-dimethyl-1,3-dithiolium) (81)[112-114] and 4,4'-biphenyl-bis(4,5-dimethyl-1,3-dithiolium) (82) dications. The 2,7-naphthalene derivative (26) [an isomer of (80)] had been previously prepared in our laboratory[69]. Our synthesis of

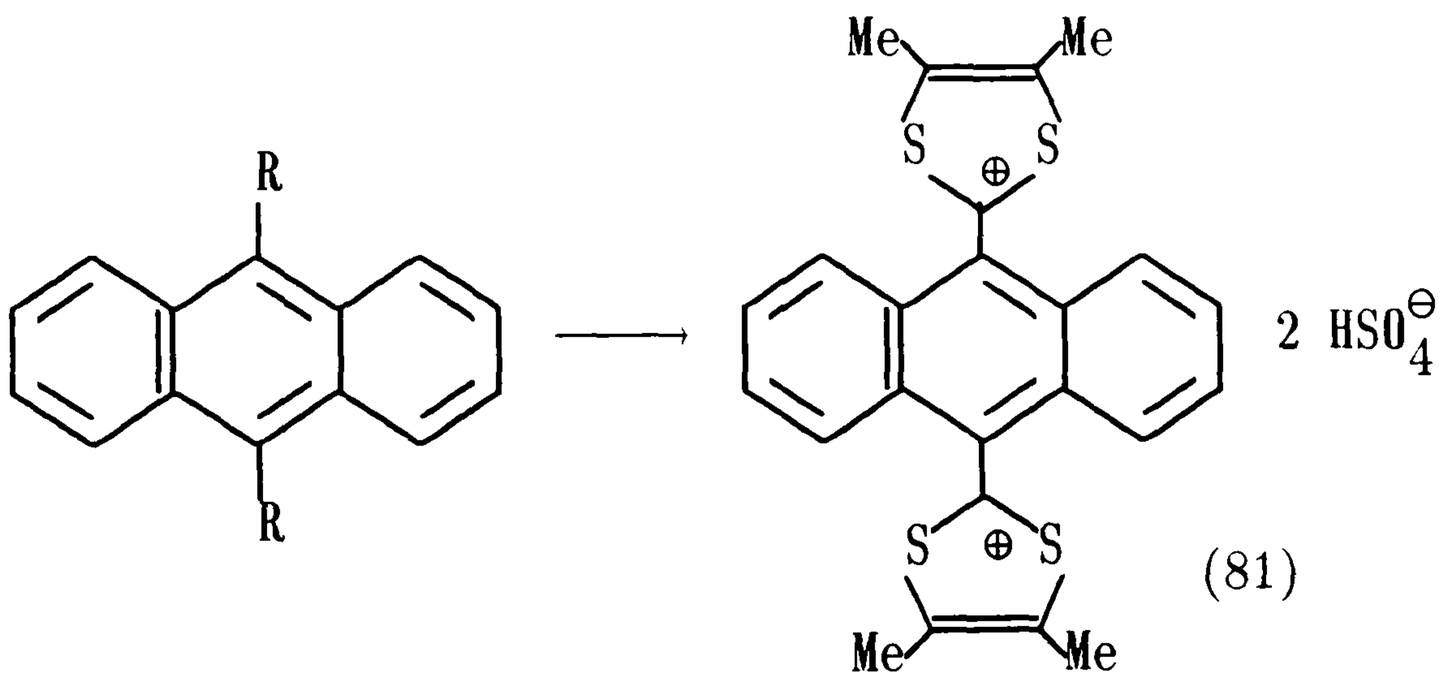
dication (80) (Scheme 2.7)[112,113] followed the route used previously for dication (26)[69] (see also Scheme 2.2).



Scheme 2.7: *Reagents: (a) NaOMe, S_8; (b) HCl; (c) piperidine; (d) MeC(=O)CHClMe; (e) conc. H_2SO_4; (f) HPF_6.*

Treatment of the known 1,4-di(bromomethyl)naphthalene (83)[115] with elemental sulphur and sodium methoxide in refluxing methanol under nitrogen using the method of Becke[116] yielded, after acid work-up, the expected bis(dithiocarboxylic acid); this pungent purple material was found to be air unstable, but was conveniently isolated and purified as the orange di(piperidinium) salt (84) (55% yield). The presence of the CS_2^- group in salt (84) was confirmed by a band in the IR spectrum at 1012 cm^{-1}. Room temperature alkylation of salt (84) with 2 mol equivalents of 3-chloro-2-butanone in methanol proceeded smoothly to afford the red bis(dithioester) (85) (63% yield, $\nu_{C=O}$ = 1700 cm^{-1}). Careful dissolution of dithioester (85) in concentrated sulphuric acid under stringently controlled conditions (-10°C) caused a rapid exothermic

dehydrative cyclisation to the bis(1,3-dithiolium)di(hydrogensulphate) salt (80a), which was conveniently precipitated as a yellow-orange solid on dilution with ethyl acetate, or acetone (92% yield). If the temperature of this reaction was allowed to rise above -5°C, complete degradation of either the starting material or the products occurred and no isolable products were obtained. The absence of a carbonyl stretching frequency in the IR spectrum of salt (80a) confirmed cyclisation of both ester groups. The salt (80a), as precipitated, was found to be analytically impure and was conveniently purified by conversion to the corresponding bis(hexafluorophosphate) salt (80b), by reaction with hexafluorophosphoric acid in water (88% yield). The overall yield for the four-step conversion of (83) into salt (80b) is 27%.



(81)

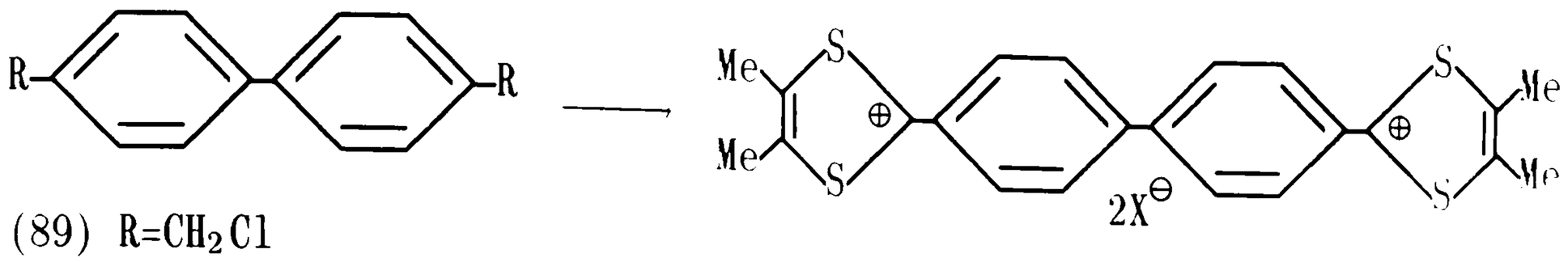
(86) R=CH_2Cl

(87) R=CS_2^-;(piperidinium$^+$)$_2$

(88) R=C(=S)SCH(Me)COMe

Scheme 2.8: *Reagents: As for Scheme 2.7; overall yield = 42%*

In an analogous series of reactions, the salts (81) (Scheme 2.8)[112-114] and (82) (Scheme 2.9) were prepared from 9,10-di(chloromethyl)anthracene (86)[117] and 4,4'-di(chloromethyl)biphenyl (89) respectively. It is noteworthy that the di(hydrogensulphate) salt (81) is extremely insoluble in most solvents, and in contrast to salts (80a) and (82a), the HSO_4^- anions could not be exchanged.



(89) R=CH_2Cl

(90) R=CS_2^-;(piperidinium$^+$)$_2$

(91) R=C(=S)SCH(Me)COMe

(82a) X=HSO_4^-

(82b) X=PF_6^-

Scheme 2.9: *Reagents: As for Scheme 2.7; overall yield = 42%*

The methyl protons of dication salts (80)-(82) are observed in the ^{1}H NMR spectrum at δ_H = 2.97, 3.01 and 2.93 ppm, respectively. This significant downfield shift from that normally observed for CH_3-C=C protons (typically δ_H = 1.6 - 2.1 ppm) is fully consistent with the cationic dithiolium structures assigned to salts (80)-(82).

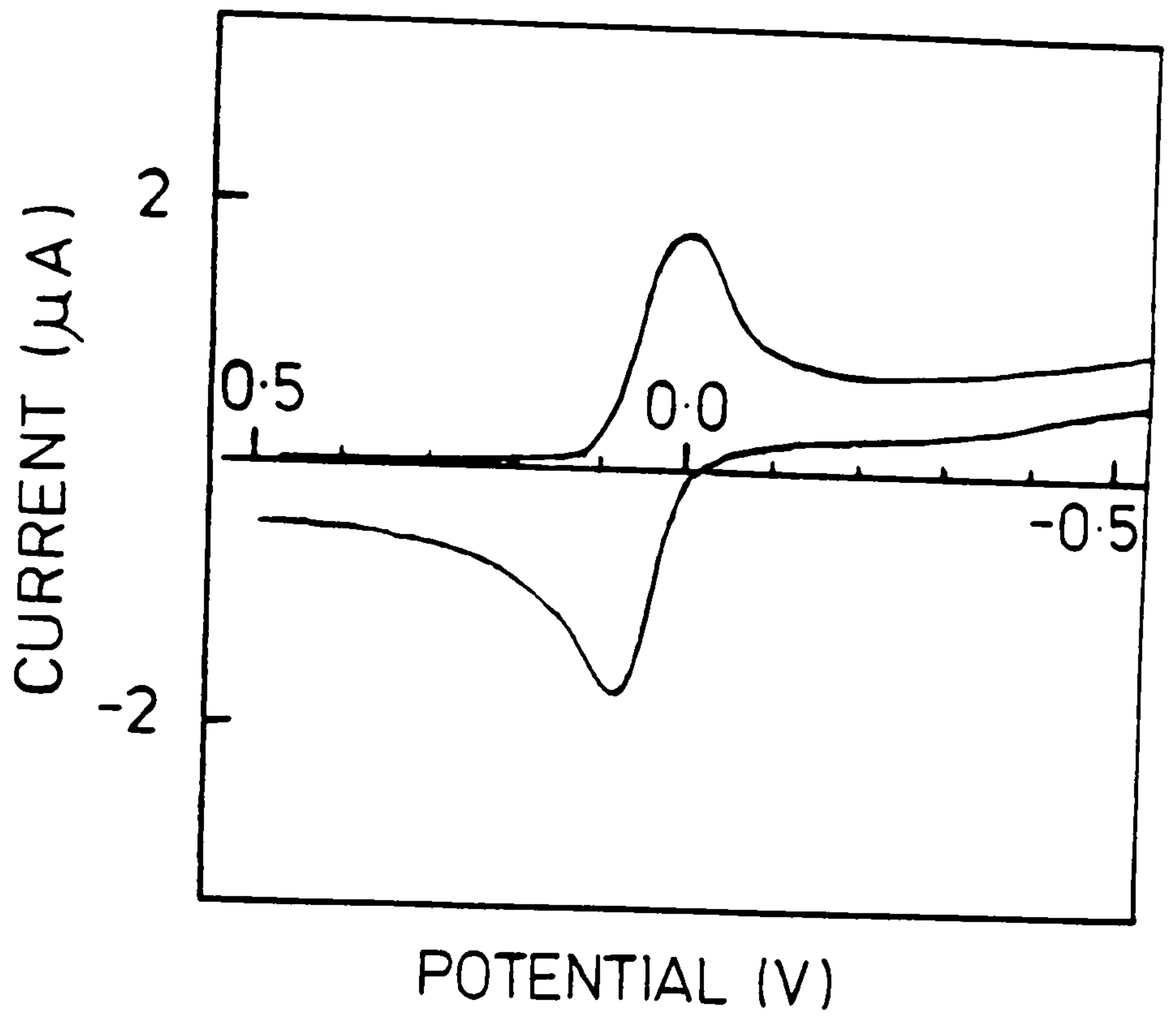
2.3.2 Cyclic Voltammetry of Dications (80) and (82)

The electrochemical reduction of dications (80) and (82) has been studied by cyclic voltammetry [Figures 2.1(a) and (b) respectively]: the data are summarised in Table 2.1, along with CV data for TTF (2), TMTTF (3), DBTTF (5) and donor (25) for comparison. The extreme insolubility of dication (81) precluded investigation of its redox behaviour.

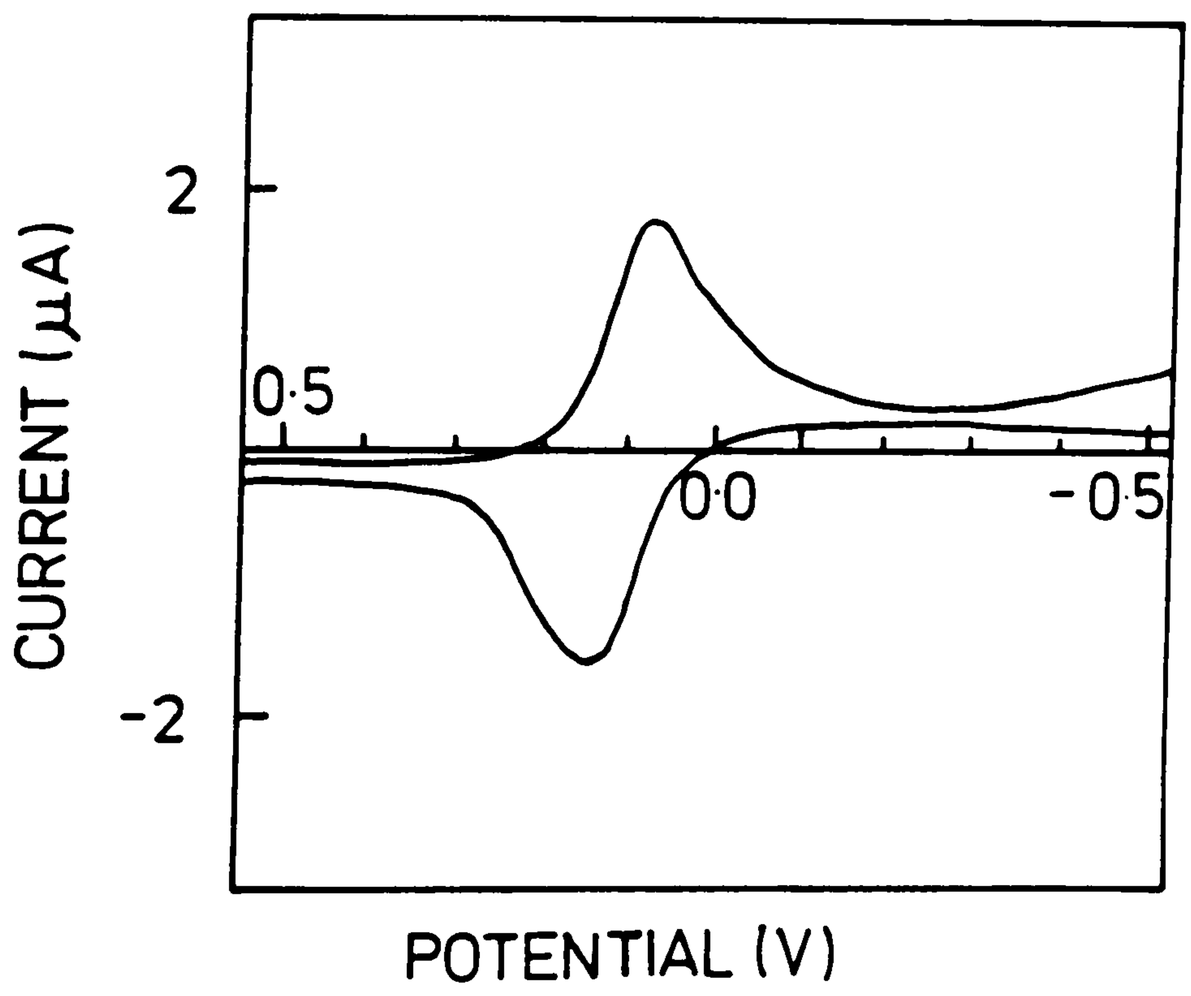
Dications (80) and (82) exhibit single reversible two-electron reductions[1] to the neutral donors at $E^{\frac{1}{2}}$ = 0.05 (Figure 2.1a) and 0.11 V (Figure 2.1b) respectively.

---

[1] anodic-cathodic peak separation of *ca.* 30mV established a reversible two-electron process.



(a)



(b)

Figure 2.1: *Cyclic Voltammogram of (a) dication (80) and (b) dication (82).*

COMPOUND		$E_1^{\frac{1}{2}}$		$E_2^{\frac{1}{2}}$
Salt	(80)[a]		0.05(2e)	
Salt	(82)[a]		0.11(2e)	
TTF	(2)[b]	0.34		0.71
TMTTF	(3)[c]	0.32		0.70
DBTTF	(5)[d]	0.61		0.93
Donor	(25)[e]		0.27(2e)	

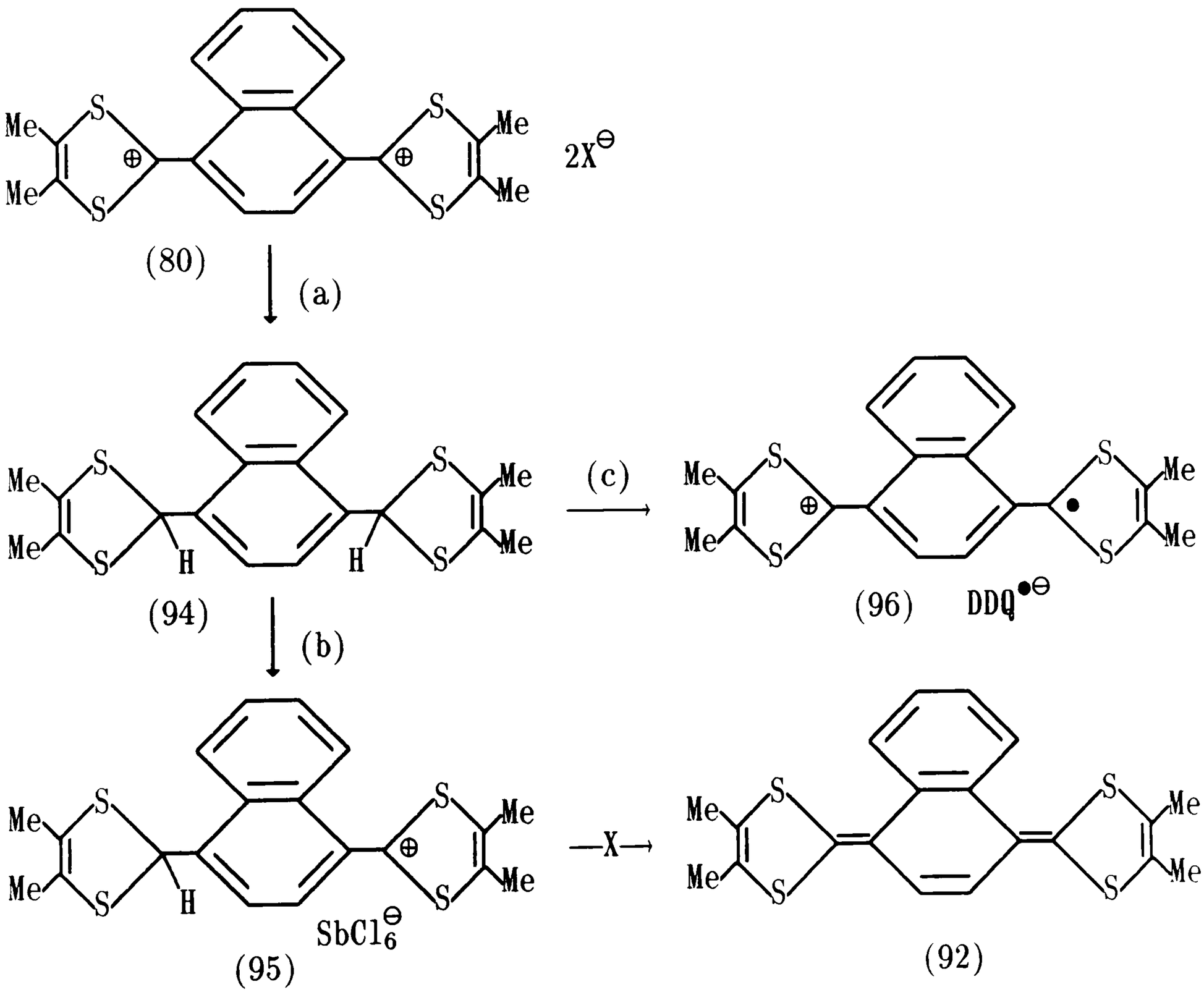
Table 2.1: *Cyclic voltammetric data; (a) This work, vs Ag/AgCl, Pt button electrode, scan rate = 100 mV sec^{-1}, 5 x 10^{-5} M dication, 0.1M $[Bu_4N][ClO_4]$ in MeCN; (b) ref.77; (c) ref.21; (d) ref.79; (e) ref.68.*

The coalescence of the two single electron waves characteristic of TTF and TMTTF into one, two-electron, redox couple as we observe for dications (80) and (82), has precedent in donor systems with a similar conjugation length between the 1,3-dithiole rings; this is attributed to reduced intramolecular Coulombic repulsion in the dicationic state[65,68,70,73]. Reduction of the dications (80) and (82) to the neutral donors, (92) and (93), occurs at E_p = 0.034 and 0.095 V, respectively. This process occurs at a considerably lower potential than the first reduction potential for TTF ($TTF^{2+} \rightarrow TTF^{+}$, E_p 0.68 V) demonstrating the increased stability of the dicationic states, (80) and (82), relative to TTF^{2+}. Furthermore, since donor strength increases as $E_1^{\frac{1}{2}}$ decreases, it is apparent that (92) and (93) are more efficient donors than TTF. Indeed, the decrease in ionisation potential for naphthoquinonoid extension of TMTTF to give (80) is similar to that observed for the known naphthoquinonoid analogue of DBTTF (5), *viz.* donor (25).

2.3.3 Attempts to Synthesise Neutral Donor (92) from Dication (80)

The CV data obtained for dications (80) and (82) suggested that their corresponding neutral donors (92) and (93) may be stable, isolable compounds. Encouraged by this, we investigated a chemical conversion of salt (80b) to neutral donor (92). An electrochemical reduction of dication (80) was not attempted.

Reduction of dication (80b) with 2 mol equivalents of sodium borohydride in ethanol gave the dihydro-derivative (94) (58% yield) (Scheme 2.10). There is considerable literature precedent for hydride abstraction, followed by deprotonation, of compounds analogous to (94) to yield neutral quinonoid donors[65,68,69,76].



Scheme 2.10: *Reagents: (a) $NaBH_4$; (b) $Ph_3C^+SbCl_6^-$; (c) 2 mol equivalents of DDQ.*

Thus, reaction of compound (94) with 1 mol equivalent of triphenylmethylhexachloroantimonate in dichloromethane at room temperature gave the monocation (95) (75% yield). However, attempts to further convert cation (95) to the neutral donor (92) by reaction with an excess of triethylamine, gave a complex mixture of products from which nothing could be isolated. It is unclear why we could not isolate the neutral species (92) from its mono-cation (95). Significantly, the analogous conversions which have been successful are all based on 1,3-benzodithiolium derivatives of (92)[65,68,69,76], where the benzo groups may contribute a significant degree of resonance stabilisation to the quinonoid state and, hence, provide a lower energy pathway for the reduction.

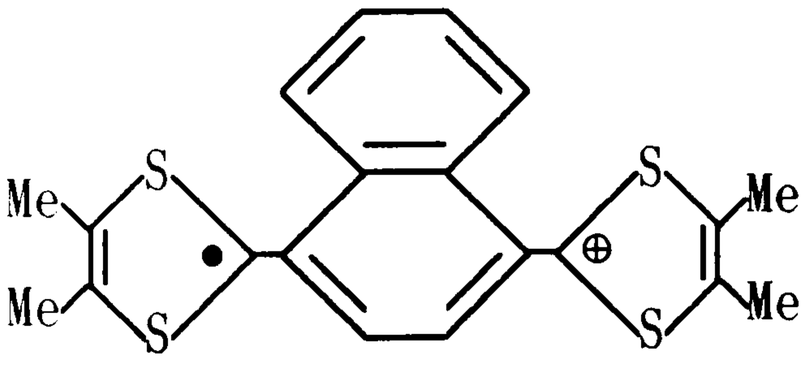
Alternative dehydrogenation of compound (94) with 2 mol equivalents of 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) in refluxing benzene afforded a highly insoluble brown powder, which was identified from analytical and spectroscopic data as a 1:1 complex of the quinol radical anion and the radical cation, (96) (20% yield). The formation of (96) can be explained by the initial dehydrogenation of (94) to yield the donor (92), which then forms a C-T complex *in situ* with a second DDQ molecule[65].

The IR spectrum of the DDQ complex (96) exhibits the expected phenoxy radical-anion band (ν_{max} = 1566 cm^{-1}) and a broad charge-transfer band (3400-3000 cm^{-1}). The almost complete disappearance of the characteristic carbonyl absorption of DDQ (ν_{max} = 1670 cm^{-1}) indicates there is almost complete one-electron transfer from the donor (92) to DDQ; consistent with this, the complex (96) is an insulator (σ_{rt} = 2 x 10^{-8} S cm^{-1}, two-probe compressed pellet measurement). Similar data have been used to identify the quinol complexes of bis(1,3-dithioles) (23)[65] and (26)[69].

2.3.4 Metathesis Reactions of Dications (80) and (82)

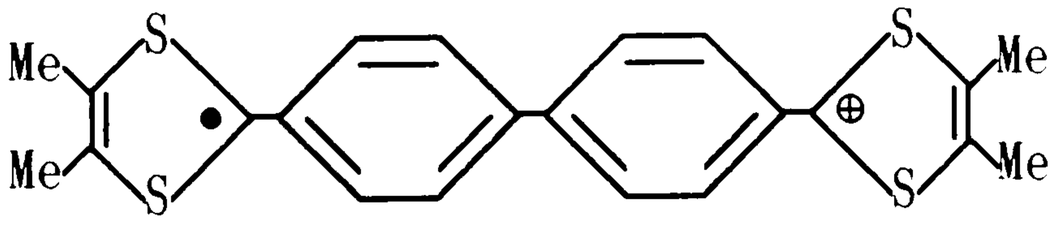
In situations where the neutral donor is not obtainable from its dication salt, complexation of the donor may effectively be achieved by metathesis reaction of the dication salt with either lithium iodide or the lithium salt of TCNQ (Li^+TCNQ^-). Such metathesis reactions have been rationalised by initial single electron transfer from I^-, or $TCNQ^-$, to the dithiolium dication, followed by aggregation of the iodine or TCNQ moiety[64]. In this way non-stoichiometric C-T complexes have often been isolated.

On addition of dication (80) to a boiling solution of excess lithium iodide in acetone, the solution immediately darkened and a fine red powder precipitated on cooling. The ratio donor : iodine for the isolated complex (97) was estimated to be 1 : 2.8 from elemental analysis. Conductivity measurements on a powdered sample showed the material to be an insulator ($\sigma_{rt} \sim 1 \times 10^{-12}$ S cm^{-1}, two-probe compressed pellet measurement).



(97) $(I_n)^{\ominus}$ n=2.8

(98) $(TCNQ)_n^{\bullet\ominus}$ n=2.4



(99) $(TCNQ)_n^{\bullet\ominus}$ n=2

Dication (80) reacted readily with an excess of Li^+TCNQ^- in boiling acetonitrile/acetone (9:1 v/v) to give a blue-black solid on cooling, which was identified from elemental analysis as complex (98) (45% yield). The stoichiometry of complex (98) is 1 : 2.4 (donor : TCNQ) and was highly reproducible on several samples. Similarly, dication (82)

reacted with $Li^{+}TCNQ^{-}$ in acetone to give complex (99) (40% yield, 1 : 2 stoichiometry). Both complexes (98) and (99) were only isolated as amorphous powders, recrystallisation failed to yield single crystals of suitable quality for X-ray analysis. Physical data for complexes (98) and (99) are summarised in Table 2.2.

	COMPLEX	
	(98)	(99)
D:A Stoichiometry[a]	1 : 2.4	1 : 2
σ(rt) (S cm^{-1})[b]	1 x 10^{-3}	6 x 10^{-2}
ν(C≡N) (cm^{-1})[c]	2177	2183
λ(max) (nm)[d]	880, 835, 780, 380	895, 835 780, 385

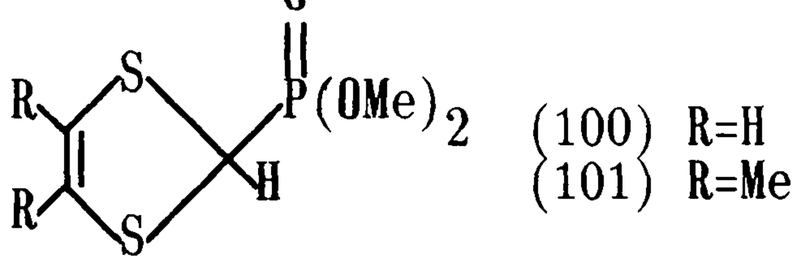
Table 2.2: *Physical properties of complexes (98) and (99); (a) deduced from elemental analysis; (b) two-probe compaction measurement; (c) FT-IR (KBr disc); (d) solid-state UV-visible (Nujol, CaF_2 plates).*

Both complexes (98) and (99) exhibit two-probe compaction conductivities in the semiconductor regime, indicative of a segregated stacking motif with partial charge-transfer. Unambiguous confirmation of a segregated stack motif with partial charge-transfer for complexes (98) and (99) would require single crystal X-ray analysis. The FT-IR spectra of both complexes show broad peaks, characteristic of an organic conductor. In particular, broad charge-transfer bands and broad cyanide absorptions are observed, which are characteristic of the TCNQ radical anion[18]. Solid-state UV-visible spectra show characteristic transitions of TCNQ and $TCNQ^{\bullet -}$ [118] consistent with the complexes being mixed valence. The existence of charge-transfer in complex (98) was further confirmed from solid-state ESR measurements; these show a strong singlet with a g-value of 2.0003, indicative of an organic radical.

The extreme insolubility of dication (81) has so far precluded the characterisation of any of its complexes *via* metathesis reaction.

2.4 EXTENDED BIS(1,3-DITHIOLE) DONORS: NOVEL WITTIG-HORNER METHODOLOGY

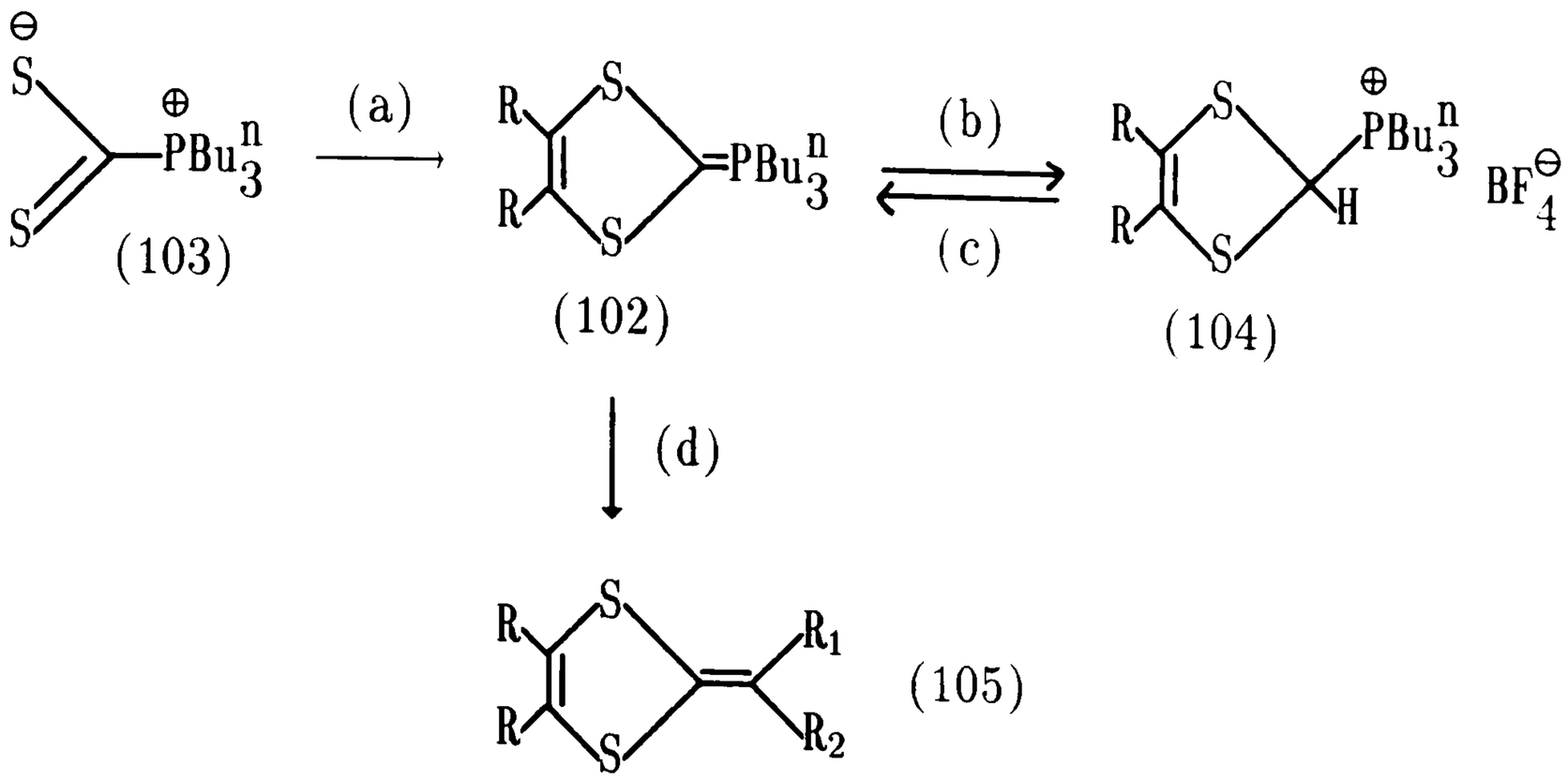
Following our investigations of the bis(4,5-dimethyl-1,3-dithiolium) dications (80)-(82), we turned our attentions to a quite different synthetic approach designed to yield extended quinonoid donors in their neutral (reduced) forms. Only a small number of neutral quinonoid bis(1,3-dithiole) donors are known and they generally have been prepared by benzene-1,2-dithiol condensation with a dialdehyde, followed by hydride and proton abstraction (Scheme 2.3). We have now developed an alternative methodology based on Wittig-Horner reactions of 1,3-dithiolephosphonate esters (100) and (101).



(100) R=H
(101) R=Me

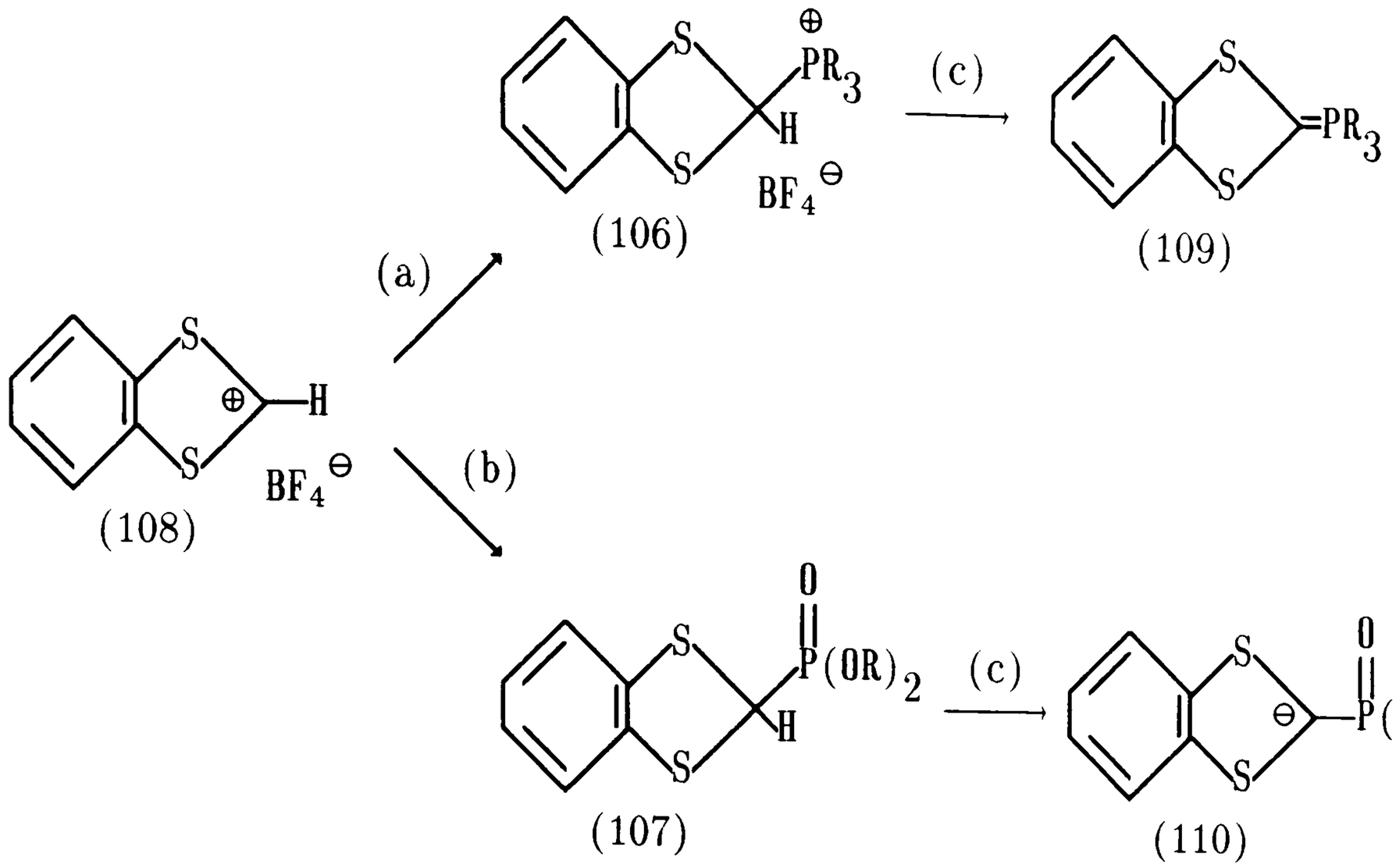
2.4.1 Wittig Methodology to 2-Alkylidene-1,3-dithiole Derivatives (105)

Initially, Hartzler reported that 1,3-dithiole-2-ylidene-tributylphosphoranes (102) were prepared *in situ* by addition of activated acetylenes to a complex of tributylphosphine and carbon disulphide (103) and that ylid (102) could be used for subsequent Wittig reaction[119]. The intermediate phosphoranes (102) can be trapped as their phosphonium salts (104) only when the acetylene bears at least one carboxylic acid group, by treatment with tetrafluoroboric acid-diethyl-etherate (Scheme 2.11)[120].



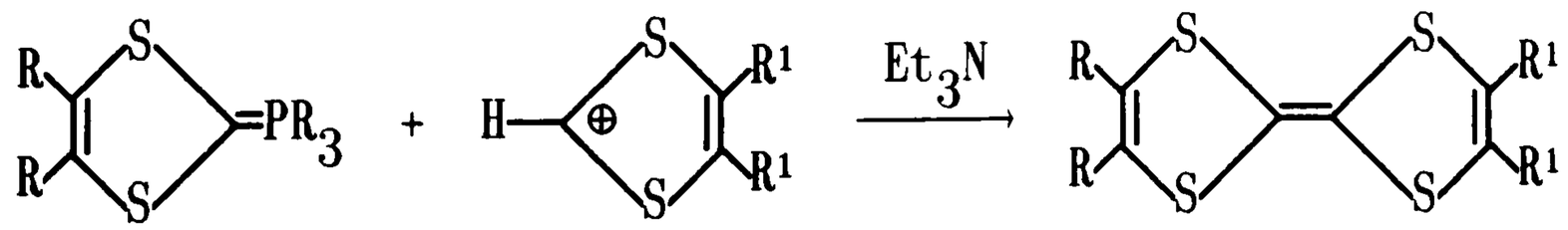
Scheme 2.11: *Reagents: (a) R–C≡C–R; (b) HBF_4; (c) n-BuLi; (d) $R_1R_2C=O$*

An extensive study of Wittig reactions of phosphorane (102, R=CO_2Me) was undertaken by Cava *et al.*[121] The intermediacy of an analogous phosphorane during desulphurisation of 4,5-dicyano-1,3-dithiole-2-thione (74, R=CN) with tertiary phosphines was reported[122]; however, a similar phosphorane has not been detected in desulphurisation of other 1,3-dithiole-2-thiones[123]. In 1976, Akiba *et al.* first demonstrated that a stable phosphonium salt (106), or a phosphonate ester (107), could be isolated by reaction of a tertiary phosphine, or a trialkylphosphite, respectively, with 1,3-benzodithiolium tetrafluoroborate (108) (Scheme 2.12)[109]. This methodology is, however, not applicable to the synthesis of phosphonium salts, or phosphonate esters, having electron withdrawing groups on the 1,3-dithiole ring since the required 1,3-dithiolium cations are not obtainable[124]. The ylids (109) and (110) derived from the phosphonium salt (106) and phosphonate ester (107), respectively, by deprotonation with a strong base, react cleanly with carbonyl compounds to give 2-alkylidene-1,3-dithioles [(105), R = $-(CH=CH)_2-$][109,125].



Scheme 2.12: *Reagents: (a) PR_3; (b) $P(OR)_3$, NaI; (c) n-BuLi.*

The phosphoranes (76) have been extensively utilised by Yoshida *et al.* in the preparation of TTF vinylogues (Scheme 2.4)[78,79]. Coupling reaction of phosphoranes (76) with 1,3-dithiolium cations (73) has been shown to yield unsymmetrical TTF derivatives (Scheme 2.13), along with other products derived from the 1,3-dithiolium cation and decomposition of the phosphorane[24,126]. However, the ylids derived from the phosphonate esters [namely (110)] have received far less attention, although Akiba *et al.* had reported their superiority over phosphoranes (109) in Wittig reactions[109].



(76) (73)

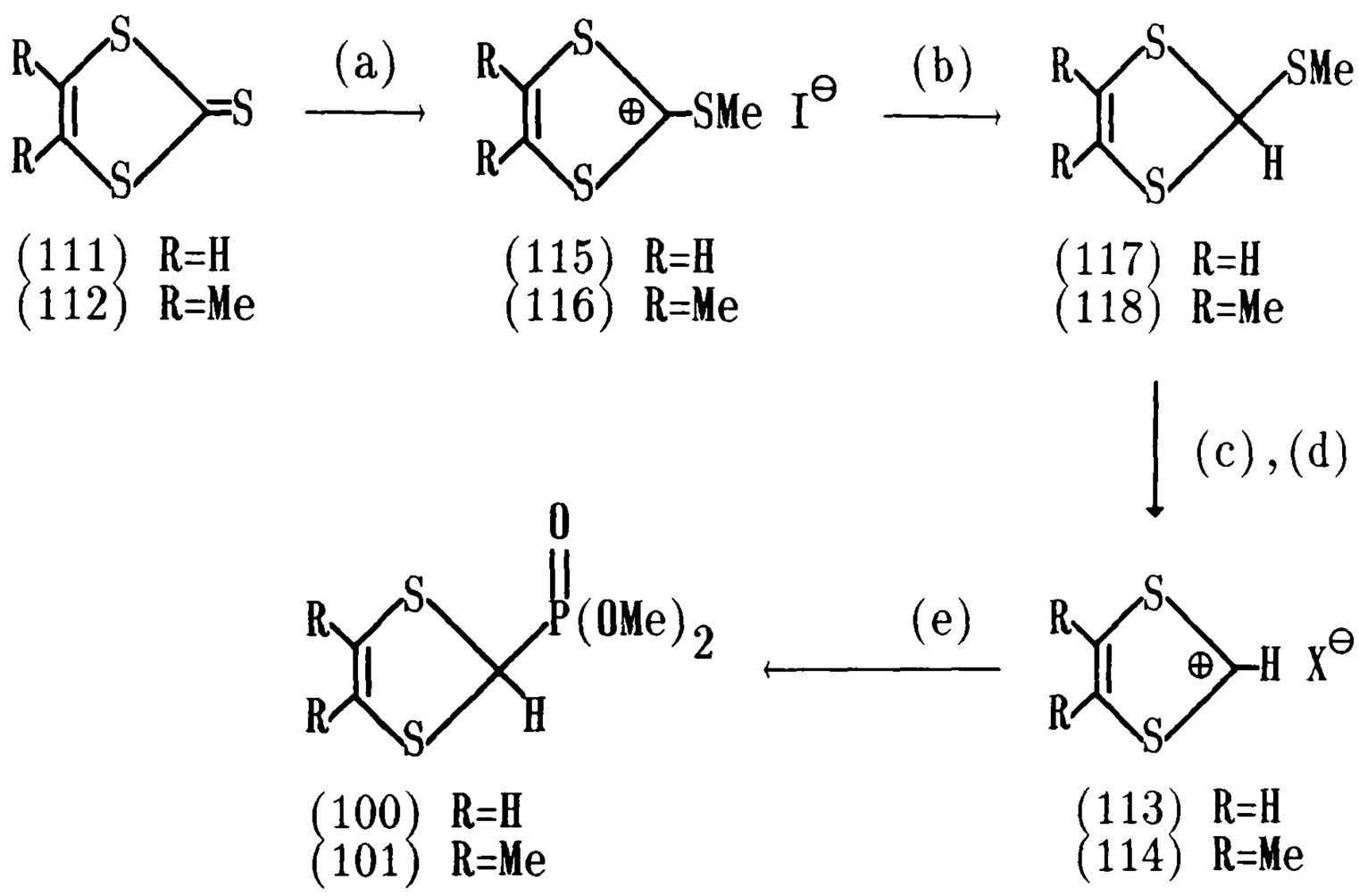
Scheme 2.13

We chose to investigate the chemistry of the known (but previously unstudied) 4,5-dimethyl-2-dimethoxyphosphinyl-1,3-dithiole (101)[109] and also the unknown parent, 2-dimethoxyphosphinyl-1,3-dithiole (100). These

esters seemed to be promising precursors to new extended quinonoid bis-(1,3-dithiole) donors. Before the outset of our work, the only extended bis(1,3-dithiole) donor realised by reaction of ylid (110) was donor (31)[73,109]; subsequently Yamashita *et al.* have reported analogous methodology to donors (33) and (34)[73].

2.4.2 Preparation of Phosphonate Esters (100) and (101)

Our synthetic approach to the phosphonate esters (100) and (101) is outlined in Scheme 2.14.



(111) R=H, (112) R=Me

(115) R=H, (116) R=Me

(117) R=H, (118) R=Me

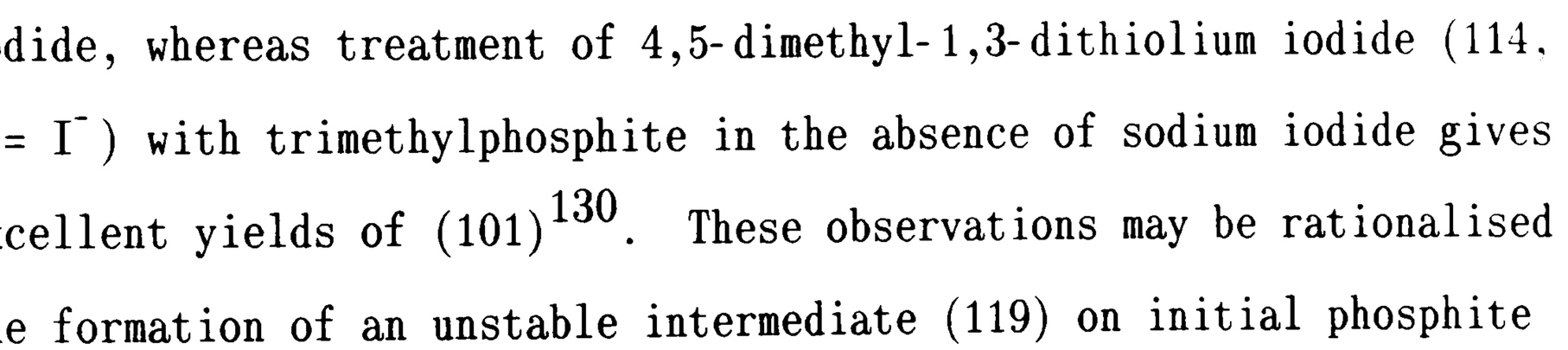
(100) R=H, (101) R=Me

(113) R=H, (114) R=Me

Scheme 2.14: *Reagents: (a) MeI; (b) $NaBH_4$; (c) AcOAc; (d) $HBF_4.Et_2O$; (e) $P(OMe)_3$, NaI.*

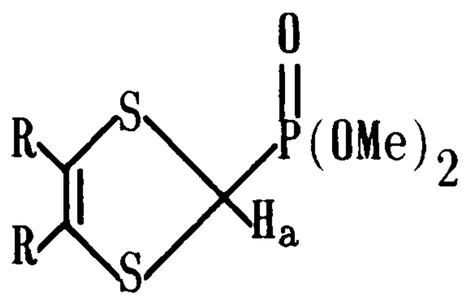
Literature routes to the thiones (111)[127] and (112)[21] were closely followed without significant modification. In our hands, the conventional peracid treatment of thiones (111) and (112) failed to give satisfactory yields of salts (113) and (114)[128]. Instead, we employed a convenient, three-step procedure first described by Wudl *et al.*[129] Alkylation at the sulphur of thiones (111) and (112) with an excess of methyl iodide in nitromethane gave the corresponding 2-methylthio-1.3-

dithiolium iodides (115) and (116), respectively, in quantitative yields. Reduction of the methiodides (115) and (116) with one equivalent of sodium borohydride in methanol at $0^{o}C$ proceeded vigorously to give (117) and (118), respectively, as yellow oils (>90% yield). Further reaction of (117) and (118) with acetic anhydride, followed by addition of tetrafluoroboric acid-diethyletherate and anhydrous ether precipitated the desired salts (113, X = BF_4^-) and (114, X = BF_4^-) in excellent purity as white solids (95% yield). The salts (113) and (114) decomposed on standing at room temperature, but could be conveniently stored at $-20^{o}C$ for long periods without significant decomposition. The salts (113) and (114) reacted rapidly with freshly distilled trimethylphosphite in the presence of an equimolar amount of sodium iodide in dry acetonitrile under nitrogen at room temperature to give the phosphonate esters (100) and (101) in quantitative yields. It is notable that the reaction does not occur in the absence of sodium iodide, whereas treatment of 4,5-dimethyl-1,3-dithiolium iodide (114, X = I^-) with trimethylphosphite in the absence of sodium iodide gives excellent yields of (101)[130]. These observations may be rationalised by the formation of an unstable intermediate (119) on initial phosphite attack on the cation; iodide ions then displace one methyl group in an energetically favourable formation of a stable phosphorus-oxygen double bond - a Michaelis-Arbuzov type reaction (Scheme 2.15).



Scheme 2.15

The phosphonate esters (100) and (101) are both isolated as hygroscopic thick red oils and could easily be purified by dry column chromatography (neutral alumina, ethyl acetate) - elemental analysis. IR, ^{1}H NMR and mass spectra were consistent with their structures. Both esters (100) and (101) exhibited strong absorptions characteristic of P=O (1240-1260 cm^{-1}) and P-O-C (1030-1050 cm^{-1}) stretching vibrations in the infrared, and they showed the parent peak (M^{+}) in the mass spectrum along with a base peak assignable to M^{+}-P(=O)(OMe)$_2$. NMR data are summarised in Table 2.3.

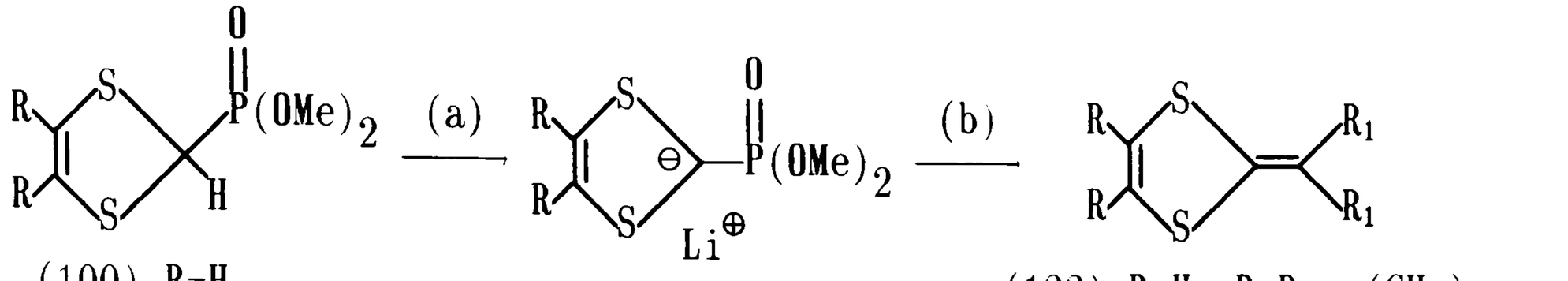


FRAGMENT	(100) R = H	(101) R = Me
R	5.98 (2H,s)	1.86 (2H,s)
H_a	4.73 (1H,d,J=4.5 Hz)	4.75 (1H,d,J=4.5 Hz)
OMe	3.75 (6H,d,J=10.5 Hz)	3.80 (6H,d,J=10.4 Hz)

Table 2.3: *^{1}H NMR data for phosphonate esters (100) and (101); δ(H), solvent $CDCl_3$.*

2.4.3 Wittig-Horner Reaction of Phosphonate Esters (100) and (101)

Phosphonate esters (100) and (101) were easily deprotonated with 1 mol equivalent of n-butyllithium in THF under nitrogen at -78^{o}C; an instant colour change from red to yellow-orange was observed on dropwise addition of base to solutions of (100) and (101). The carbanions (120) and (121) thus formed underwent Wittig-Horner reaction with a variety of carbonyl compounds, such as cyclopentanone and benzophenone, to give the expected 1,3-dithiole-2-ylidene products, (yields typically 60-80%) (Scheme 2.16).



(100) R=H
(101) R=Me

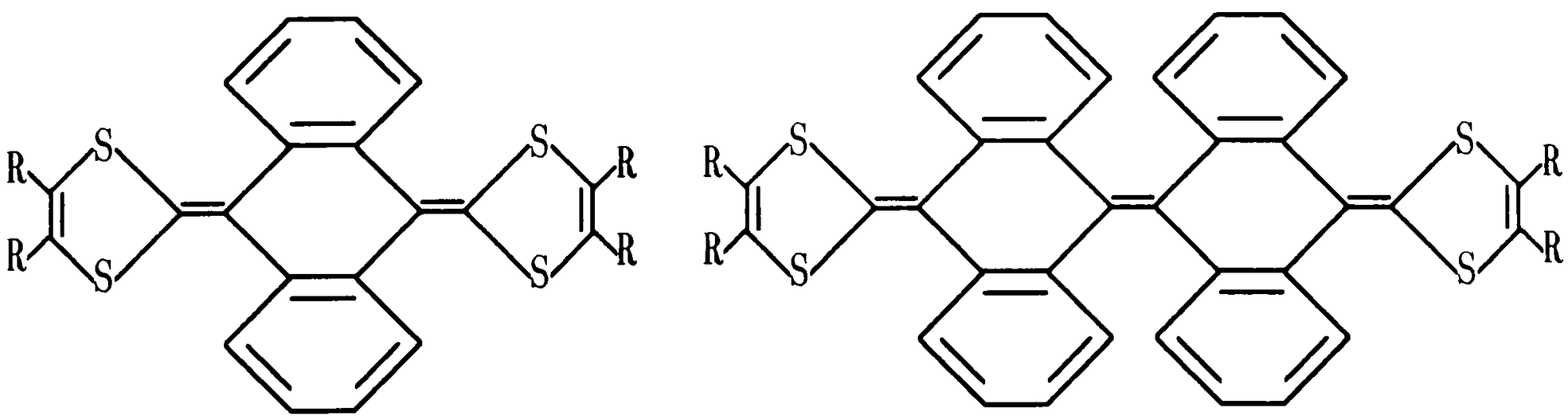
(120) R=H
(121) R=Me

(122) R=H, R_1R_1 =$-(CH_2)_4-$
(123) R=H, R_1 =Ph
(124) R=Me, R_1R_1 =$-(CH_2)_4-$
(125) R=Me, R_1 =Ph

Scheme 2.16: *Reagents: (a) n-BuLi; (b) $R_1R_1C=O$.*

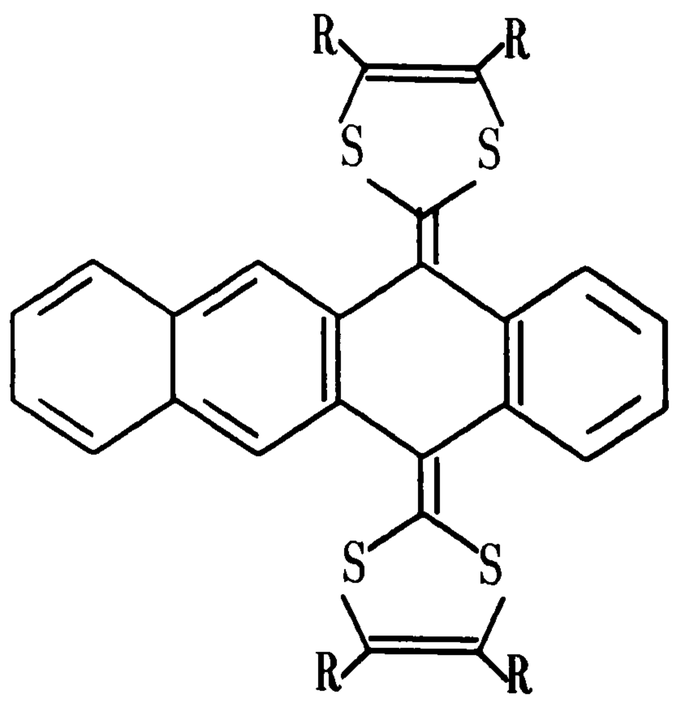
Reaction of the ylids occurred very rapidly to give dark red solutions; this high reactivity can be attributed to the fact that the phosphonate carbanions (120) and (121) are anti-aromatic (8π) systems, which endows them with strong nucleophilicity.

In our search for new extended bis(1,3-dithiole) donors, we treated 2 mol equivalents of the carbanions (120) and (121) with a number of quinones. Rapid Wittig-Horner reaction took place to give the expected symmetrical donors in good yields. The carbanions (120) and (121) reacted with anthraquinone, bianthrone and 5,12-naphthacenequinone to give the products (126)-(131). All products gave correct elemental analysis; ^{1}H NMR and mass spectra were consistent with the assigned structures.



(126) R=H, λ(max)=415
(127) R=Me, λ(max)=433

(128) R=H, λ(max)=438
(129) R=Me, λ(max)=447

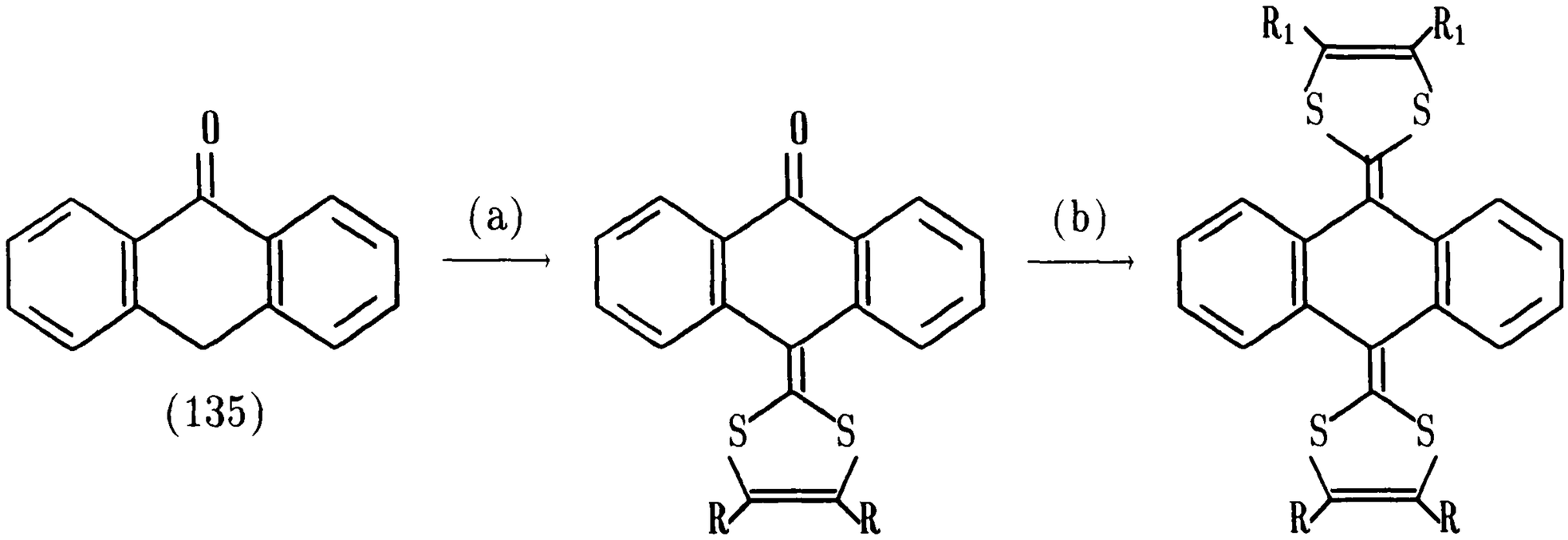


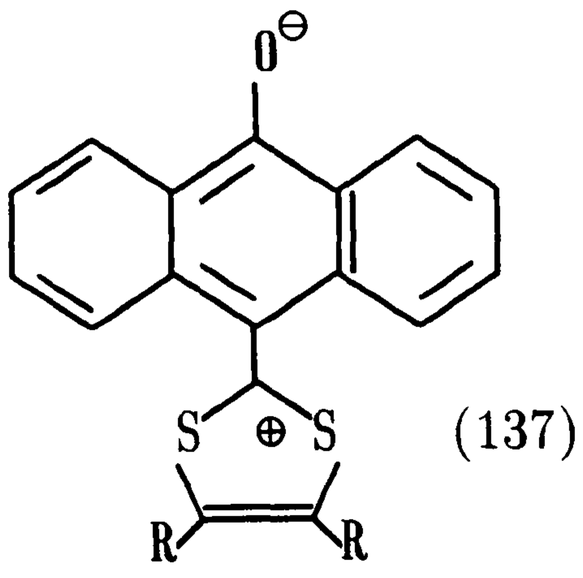
(130) R=H, λ(max)=417
(131) R=Me, λ(max)=428

Reactions of phosphonate carbanions (120) and (121) with both p-benzoquinone and 1,4-naphthoquinone gave a complex mixture of products, from which nothing could be isolated; presumably, a competing 1,4-Michael addition reaction occurs. To overcome this, reactions of carbanions (120) and (121) with duroquinone and 2,3-dimethyl-1,4-naphthoquinone were attempted; in both cases, no reaction of the starting materials was observed by TLC. This is a likely consequence of steric crowding of the carbonyl groups.

In all successful reactions, TLC investigation of the crude mixture indicated a second product, which mass spectral evidence showed to be the half-substituted quinone. These minor products could not be easily separated from unreacted starting quinone also present in the crude reaction mixture using chromatography or fractional crystallisation. An alternative synthesis of the anthraquinone derivatives (132) and (133), previously described for the synthesis of compound (134) by Gompper *et al.*, was employed[110]. Treatment of anthrone (135) with 1 mol equivalent of the 1,3-dithiolium-2-thiomethyl iodides (115) and (116) in refluxing pyridine-acetic acid (3:1 v/v) gave ketones (132) and (133), respectively, in *ca.* 85% yields (Scheme 2.17). Reaction of ketones (132) and (133) with 1 equivalent of the carbanions (120) and (121), respectively, gave the symmetrical donors (126) and (127) (*ca.* 75% yields). The asymmetrical donor (136) was easily isolated by reaction of carbanion

(120) with ketone (133), or by reaction of carbanion (121) with ketone (132) (yield *ca.* 70%). This route avoids the problems associated with traditional cross-coupling methods. This emphasises the fact that anthracenediylidene derivatives are very attractive targets for studies on unsymmetrical TTF analogues.





Scheme 2.17: *(a) Reagent (115) or (116); (b) carbanion (120) or (121).*

2.4.4 X-Ray Crystal Structure of 9,10-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (127)

The X-ray crystal structure of 9,10-bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (127)[2] reveals a highly distorted structure with the central quinonoid ring bent into a boat conformation, giving a "butterfly" arrangement (Figure 2.2).

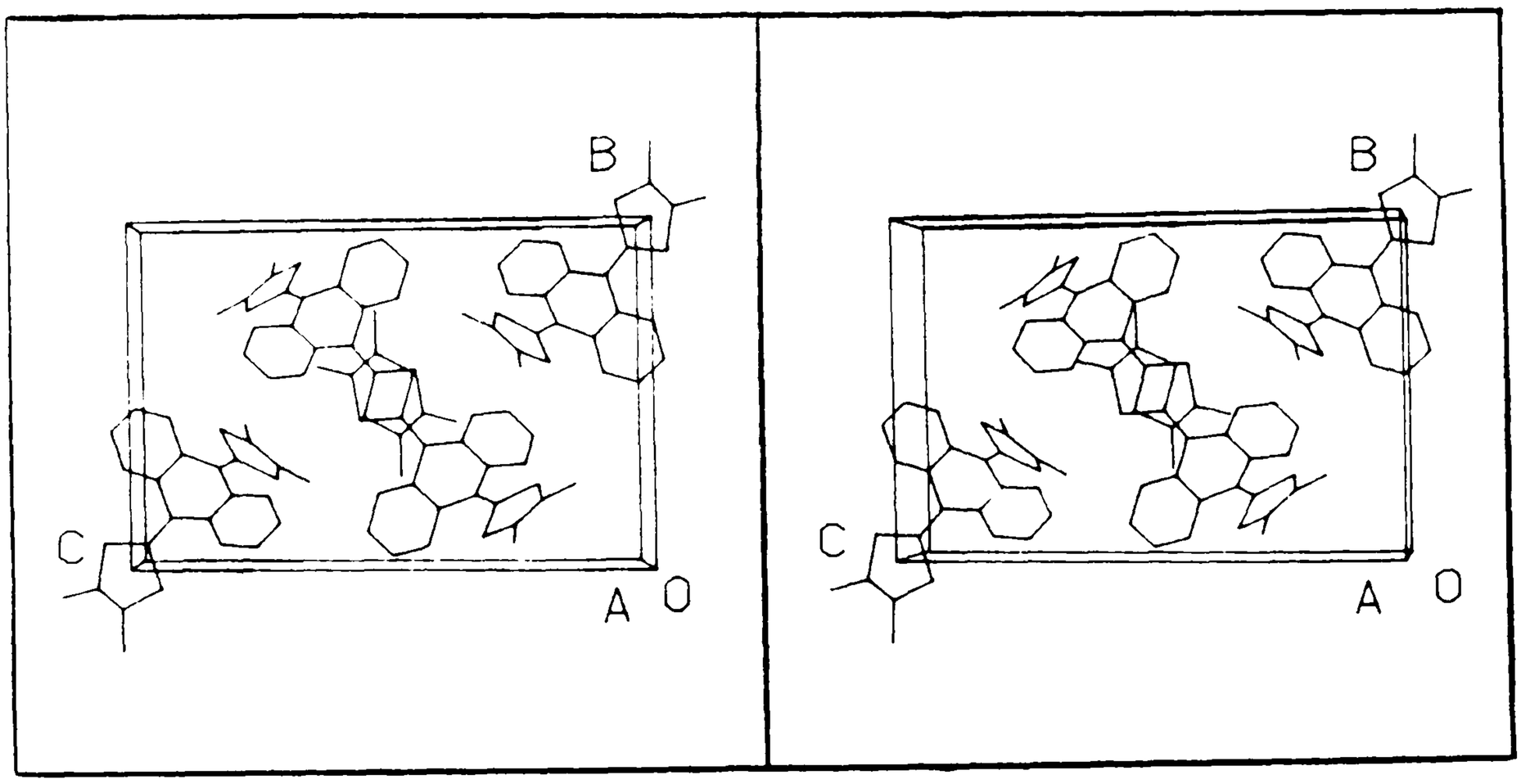


Figure 2.2: *Single crystal X-ray structure of 9,10-bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (127); Stereoview down the a-axis.*

In this way steric congestion between the peri-hydrogens and the sulphur atoms is relieved. Analogous boat-shaped quinonoid moieties are observed in the X-ray structures of the TCNQ analogue of (127), *viz.* TCNAQ (32)[75], and other sterically crowded TCNQ analogues [*eg.* Tetramethyl-TCNQ (TMTCNQ)[131]], and can be expected for all the neutral extended quinonoid donors studied here.

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[2]Crystallographic studies on donor (127) were performed by Dr. A.I. Karaulov and Prof. M.B. Hursthouse, Queen Mary College, London.

2.4.5 Optical Absorption Spectra

The solution UV-visible spectra of the extended donors (126)-(131) and (136) all show the expected bathochromic shifts relative to TTF (2) (λ_{max} = 317 nm) and TMTTF (3) (λ_{max} = 310 nm); this is consistent with a lowering of the $\pi \longrightarrow \pi^*$ excitation energy as a result of the increase in conjugation between the 1,3-dithiole rings. It is interesting that the UV spectra of ketones (132) and (133) are red-shifted further than their corresponding extended donors (126) and (127), respectively. This may be rationalised by a resonance contribution from the aromatic dipolar structure (137) to the excited states of (132) and (133), which would reduce the $n \longrightarrow \pi^*$ excitation energy. Furthermore, the carbonyl stretching frequencies of (132) ($\nu_{C=O}$ 1635 cm^{-1}) and (133) ($\nu_{C=O}$ 1645 cm^{-1}) are low, possibly due to a contribution of the dipolar form (137) to the ground states of (132) and (133). However, the contribution of (137) to the ground states of (132) and (133) is minimal as judged by ^1H NMR. For example, the ^1H chemical shift data for the methyl protons of (127) and (133) are virtually identical, supporting canonical form (133) for the ketone [*viz.* δ_H ($CDCl_3$) = 1.91 ppm for (127), 1.98 ppm for (133)]. A methyl substituent on a cationic 1,3-dithiolium ring should occur at δ_H = 2.90-3.05 ppm [*cf.* dications (80)-(82)]. A similar argument may be applied to ketone (132).

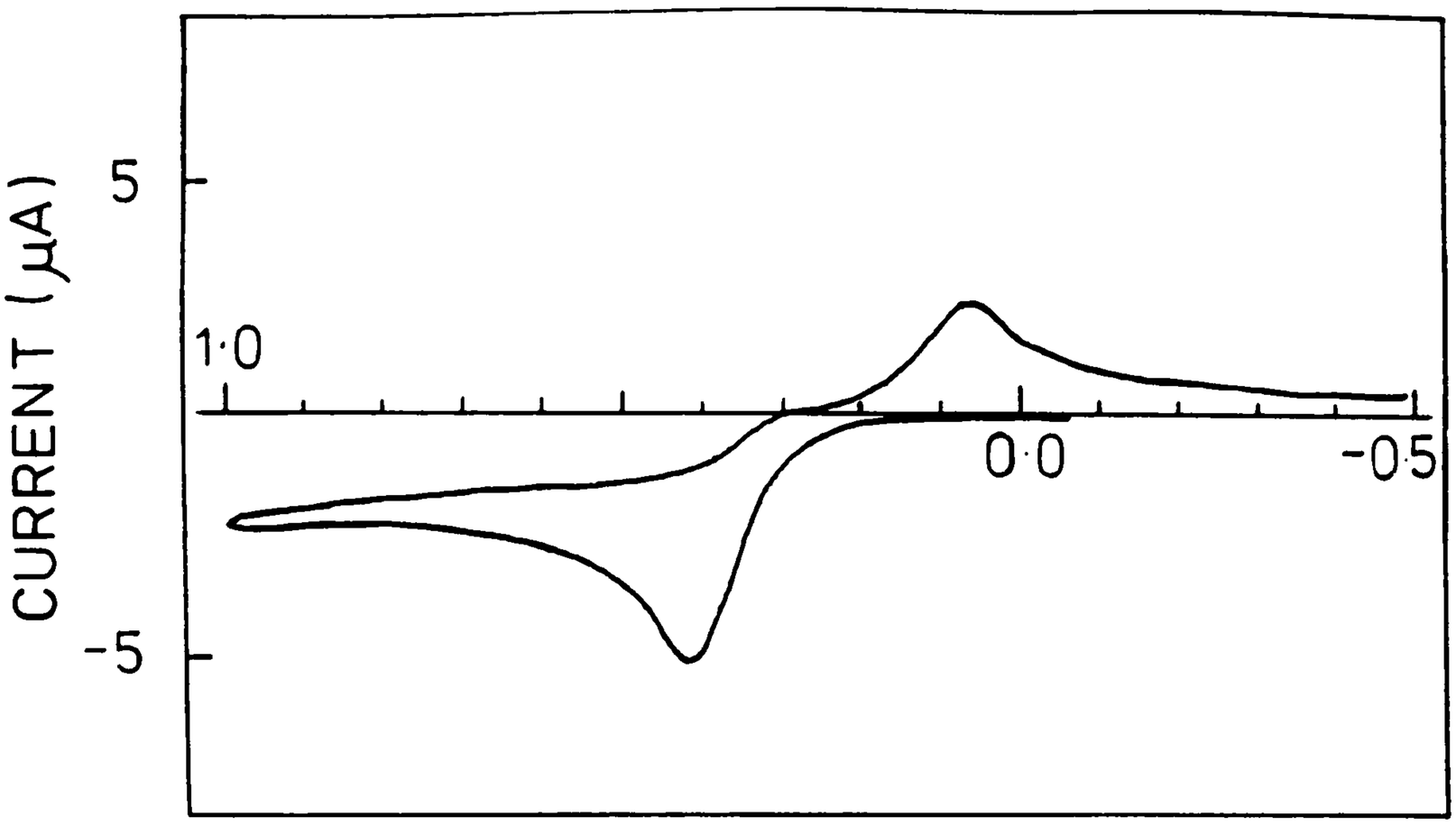
2.4.6 Cyclic Voltammetry

The electrochemical redox behaviour of the new donors (126)-(131) and (136) has been studied by CV and results are summarised in Table 2.4.

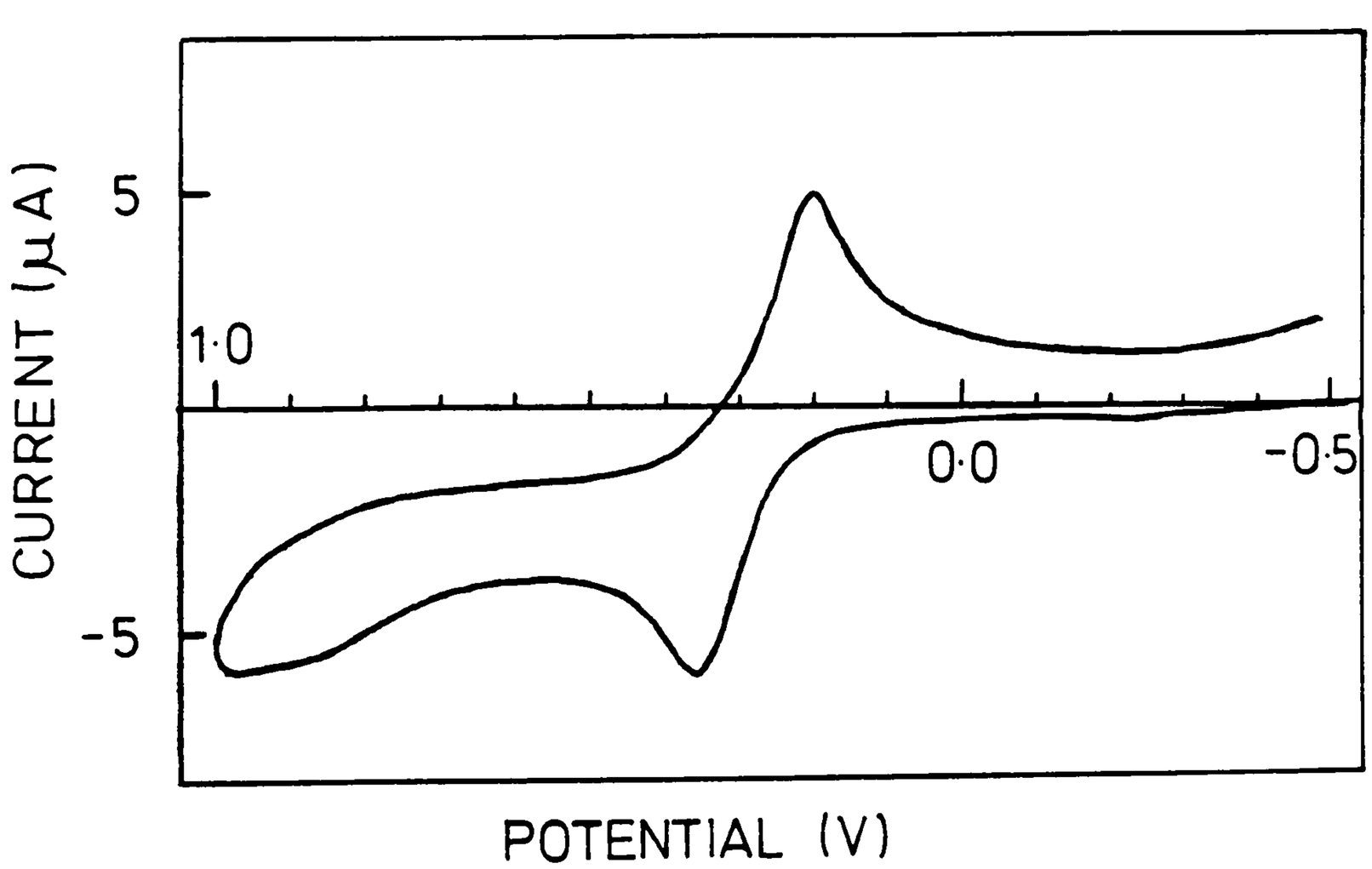
DONOR	E_{ox}	E_{red}
(126)	0.40	0.20
(127)	0.42	0.07
(128)	0.48	0.01
(129)	0.45	0.11
(130)	0.44	0.12
(131)	0.41	0.09
(136)	0.36	0.19

Table 2.4: *CV data for donors (126)-(131) and (136); vs Ag/AgCl. Pt button electrode, scan rate=100 mV sec^{-1}, 5 x 10^{-5} M donor, 0.1 M [Bu_4N][ClO_4] in MeCN.*

Figures 2.3(a) and (b) are representative of the cyclic voltammograms of extended bis(1,3-dithiole) donors (126)-(131) and (136). Interestingly, all donors (126)-(131) and (136) show only one oxidation process. This was confirmed to be a two-electron process by coulometric analysis [for donor (127)]. The separate oxidation peaks could not be resolved by reducing the scan rate to 10 mV sec^{-1} or by lowering the temperature to -30^{o}C for donor (127). Thus, it remains unclear as to whether the oxidation that occurs is a single, two-electron process, or two, inseparable, concurrent, one-electron processes. However, the coalescence of the two one-electron processes characteristic of TTF and TMTTF into a single oxidation wave is a clear indication that introduction of the quinonoid fragment into the TTF skeleton has decreased Coulombic repulsion in the doubly ionised state. The oxidation potentials for (126)-(131) and (136) are slightly larger than the first oxidation potentials for TTF ($E_1^{\frac{1}{2}}$ = 0.34 V) and TMTTF ($E_1^{\frac{1}{2}}$ = 0.32 V), indicating that they are poorer donors when E_1 values are considered: in all cases, the second electron is donated more readily than for TTF and TMTTF. With ionisation potentials in this range, it should be possible to form C-T complexes with donors (126)-(131) and (136).



(a)

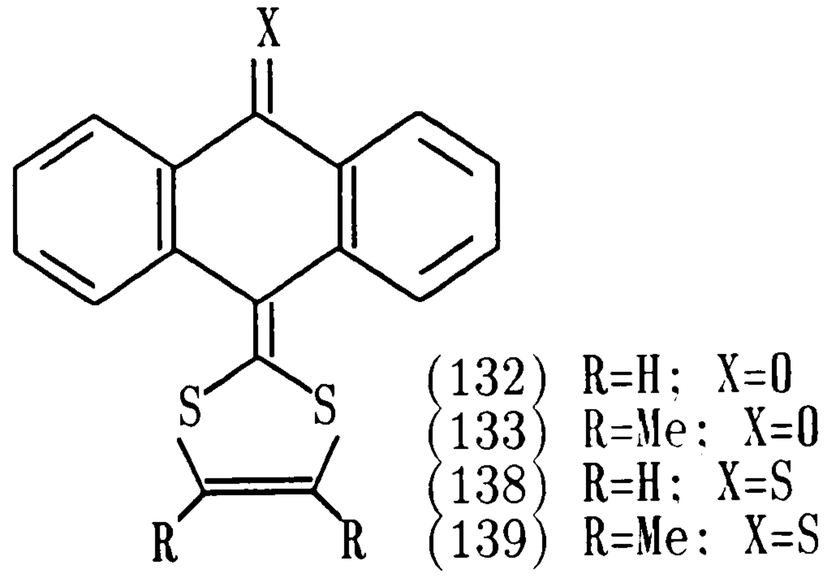


(b)

Figure 2.3: *Representative cyclic voltammograms of extended bis(1,3-dithiole) donors; (a) donor (127); (b) donor (136).*

All donors (126)-(131) and (136) show a single reduction wave at far lower potentials than expected for a reversible process. However. we tentatively assign the observed reduction wave as being associated with the process donor^{2+} $\longrightarrow$ donor, as there is no detectable change in the voltammograms after 30 minutes of continuous cycling between 0.00 V and 1.00 V. It is, however, unclear why the reduction of the dications to their corresponding neutral donors should occur at such low potentials; it may be a reflection of the stability of the formally aromatic dications, in which the central ring could gain planarity (see Chapter 2.4.8). The energy required to overcome the loss of aromaticity and form the sterically demanding quinonoid skeletons of the neutral donors may be high.

COMPOUND	$E_1^{\frac{1}{2}}$
(132)	0.85
(133)	0.79
(138)[a]	0.61
(139)[a]	0.55



(132) R=H; X=O
(133) R=Me; X=O
(138) R=H; X=S
(139) R=Me; X=S

Table 2.5: *CV data for ketones (132) and (133) and thioketones (138) and (139); vs Ag/AgCl, Pt button electrode, scan rate = 100 mV sec^{-1}, 5 x 10^{-5} M donor, 0.1M [Bu$_4$N][ClO$_4$] in MeCN; (a) oxidations completely irreversible.*

Table 2.5 contains CV data for compounds (132), (133), (138) and (139).[3] The ketones (132) and (133) show a single, cleanly reversible one-electron redox couple to the radical-cation at high potential [Figure 2.4(a) and (b) respectively], consistent with the intramolecular electron withdrawing effect of the carbonyl group. A reduction of this effect can be expected for thioketones (138) and (139): predictably.

[3]Thioketones (138) and (139) were easily prepared by reaction of ketones (132) and (133) with phosphorus pentasulphide in pyridine (ref.132).

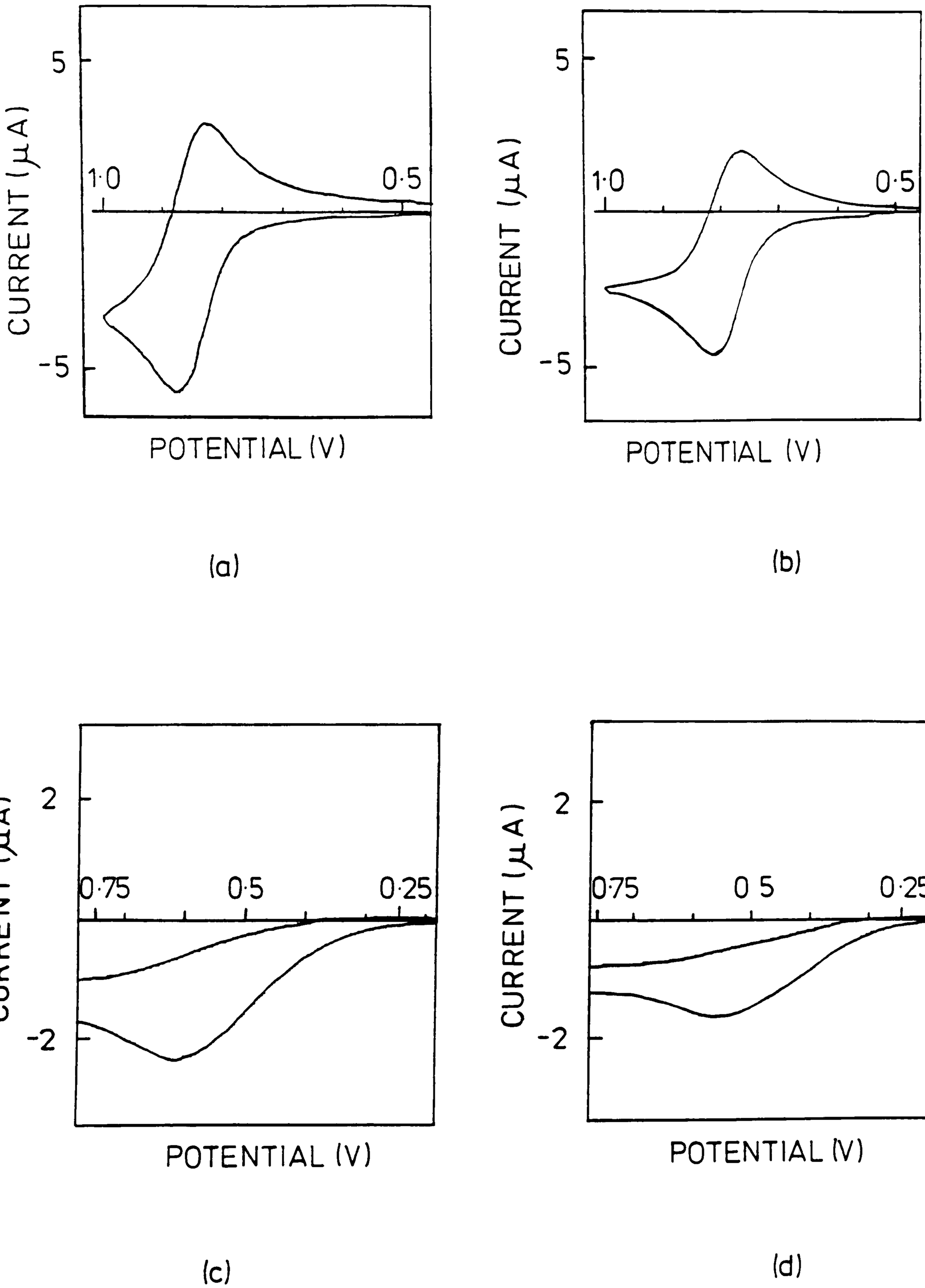


Figure 2.4: *Cyclic Voltammograms of (a) ketone (132); (b) ketone (133); (c) thioketone (138) and (d) thioketone (139).*

their oxidations occur at a lower potential than the corresponding ketones. However, to our surprise, the oxidations of thioketones (138) and (139) [Figure 2.4(c) and (d)] are completely irreversible, presumably reflecting instability in the radical-cation. Comparison of the oxidation potentials of (132), (133), (138) and (139) with the first oxidation potential of TTF ($E_1^{\frac{1}{2}}$ = 0.34 V) shows that compounds (132), (133), (138) and (139) are all far weaker donors than TTF. It is, thus, not surprising that these compounds show no tendency to form C-T complexes with TCNQ.

2.4.7 C-T Complexes of Donors (126)-(131) and (136)

We have found that donors (126)-(131) and (136) form C-T complexes with TCNQ when boiling saturated solutions of donor and TCNQ are combined and cooled; the immediate appearance of the characteristic UV absorptions of the TCNQ radical-anion in solution (λ_{max} 840, 760 and 390 nm)[133] confirms that charge-transfer from donor to TCNQ has occurred. The TCNQ complexes isolated from donors (128)-(131) did not analyse reproducibly and therefore a confident estimate of stoichiometry could not be made.

The donors (126), (127) and (136) were all found to form TCNQ complexes with the most unusual stoichiometry of 1:4 (donor : acceptor) calculated from elemental analysis. This stoichiometry was found to be extremely reproducible from numerous complexation experiments involving a variety of donor : TCNQ ratios mixed in hot acetonitrile. In all cases, the complexes (126a), (127a) and (136a) were isolated as black powders. The room temperature two-probe compaction conductivities are all in the semiconductor regime (Table 2.6). Donor (127) also forms a 1:2 complex (127b) with 2,5-dibromo-TCNQ in acetonitrile, which was

found to be a comparatively poor conductor (σ_{rt} = 7 x 10^{-6} S cm^{-1}. two-probe compaction measurement). The FT-IR spectra of complexes (126a). (127a) and (136a) are characteristic of mixed valence organic conductors[18].

	COMPLEX		
	(126a)	(127a)	(136a)
D:A Stoichiometry[a]	1 : 4	1 : 4	1 : 4
σ(rt) (S cm^{-1})[b]	4 x 10^{-3}	1 x 10^{-2}	3 x 10^{-3}
ν(C≡N) (cm^{-1})[c]	2185,2155	2187,2158	2180,2158

Table 2.6: *Physical properties of complexes (126a), (127a) and (136a); (a) deduced from elemental analysis; (b) two-probe compaction measurement; (c) FT-IR (KBr disc).*

Recrystallisation of a sample of complex (127a) produced long, thin needles suitable for four-probe single crystal conductivity measurements. The variable temperature (300-40 K) conductivity data are presented in Figure 2.5.

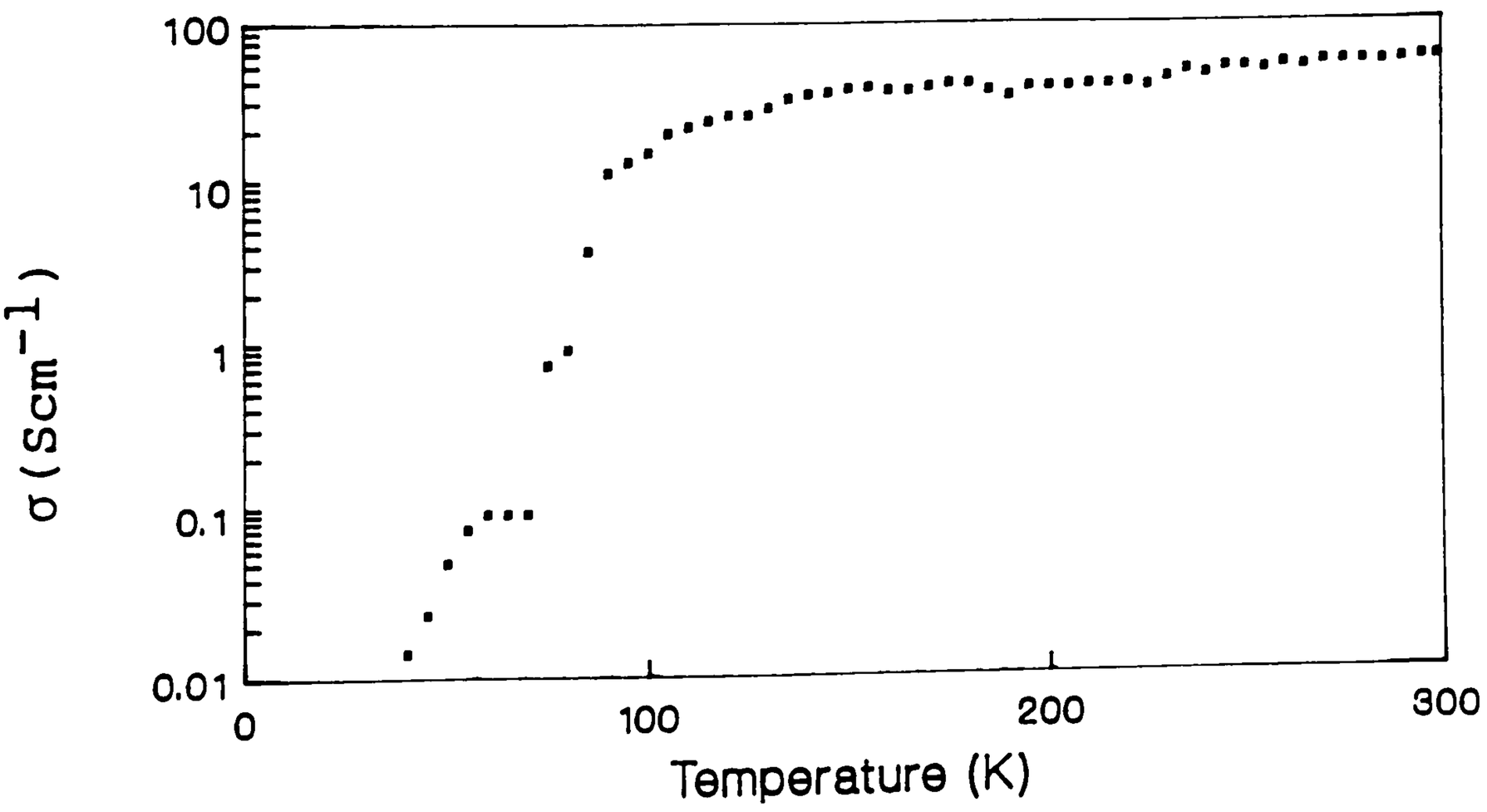


Figure 2.5: *Variable temperature conductivity data for complex (127a); four-probe, single crystal measurement; cooling run.*

The room temperature conductivity is *ca.* 60 S cm^{-1} [*cf.* the previously described powder conductivity σ_{rt} ~ 1 x 10^{-2} S cm^{-1} (Table 2.6)] and metal-like behaviour is observed over the temperature range 300-100 K, whereupon a clear transition is observed and the conductivity falls sharply. These data clearly emphasize the role that imperfect inter-particle contact can play in reducing the observed conductivity of a compaction sample relative to a single crystal[134]. Indeed, it is quite possible that complexes (126a) and (136a) may similarly exhibit metal-like conductivity in single crystal form. We note that there are very few examples of organic metals formed by complexes of this unusual 1:4 stoichiometry, one example is provided by 1,2-di(N-ethyl-4-pyridinium)-ethene (DEPE)-$(TCNQ)_4$ (σ_{rt} ~ 1000 S cm^{-1})[135].

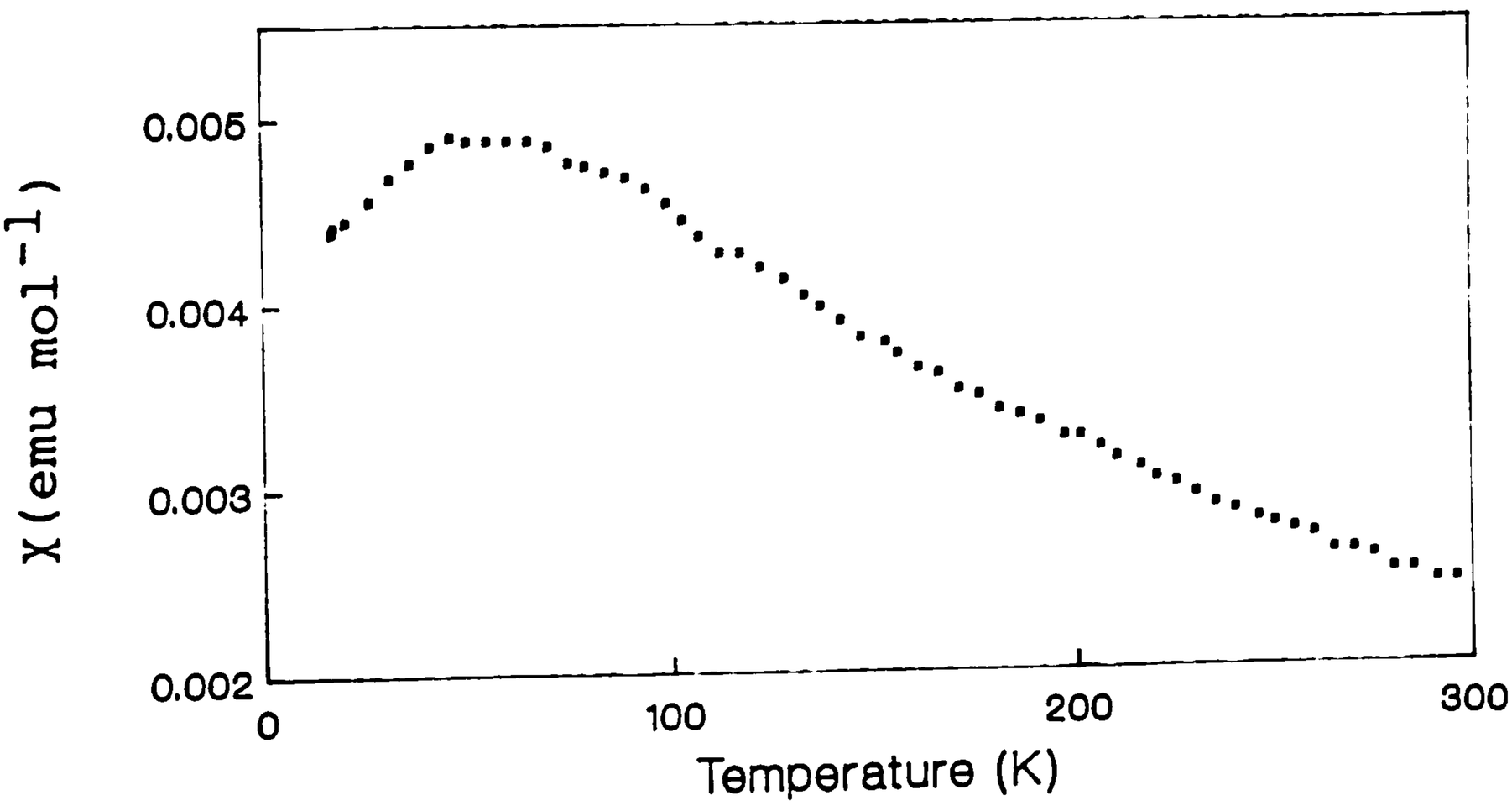


Figure 2.6: *Variable temperature magnetic susceptibility data for complex (127a).*

The variable temperature (300-4 K) static susceptibility data for complex (127a) obtained using a Faraday balance are shown in Figure 2.6[4]. The complex (127a) is paramagnetic. The susceptibility at 300 K, corrected for core diamagnetism, χ_p = 2.5 x 10^{-3} emu mol^{-1}, corresponds

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[4]Data obtained by Dr. G.J. Ashwell and A.T. Fraser, Cranfield Institute of Technology.

to an effective moment of 2.45 μ_B. This value is lower than the 2.828 μ_B required of a well developed triplet, but is in excellent agreement with μ_{eff} = 2.449 μ_B for two independent spins on the TCNQ formula unit. That is, the donor is present as the dication and there are two free electrons distributed over every four TCNQ molecules (*ie.* ρ = 0.5).

2.4.8 X-Ray Structure of Complex (127a)

The single crystal X-ray structure of complex (127a) has been successfully refined[5]. The gross structure is composed of segregated stacks of dication and TCNQ. The dication lies on a centre of symmetry in the unit cell and is surrounded by four TCNQ molecules (Figures 2.7 and 2.8). There are no short S··S intermolecular contacts between adjacent dications, the shortest being 5.170Å (*cf.* the sum of the van der Waals radii for S-S = 3.60Å)[136] implying no intermolecular donor-donor interaction. A number of short S··N contacts between the dication and TCNQ are observed (*viz.* 3.07 and 3.19Å, *cf.* the sum of the respective van der Waals radii is 3.35Å)[136].

The TCNQ molecules are planar and stack in a uniform fashion in the familiar ring-over-bond orientation[16,137], with an intermolecular stacking distance of 3.362Å, which is comparable to that found in most highly conducting TCNQ complexes (3.17 - 3.30Å)[138]. There is *no* indication of any TCNQ dimerisation within the stacks. The dimensions of the crystallographically independent TCNQ's indicate that there is partial localisation of charge onto alternate TCNQ's along the stacks.

It is fascinating to compare the conformation adopted by the dication in complex (127a) with that of the neutral donor species (127)

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[5]Crystallographic studies on complex (127a) were performed by Dr. W. Clegg, University of Newcastle-upon-Tyne.

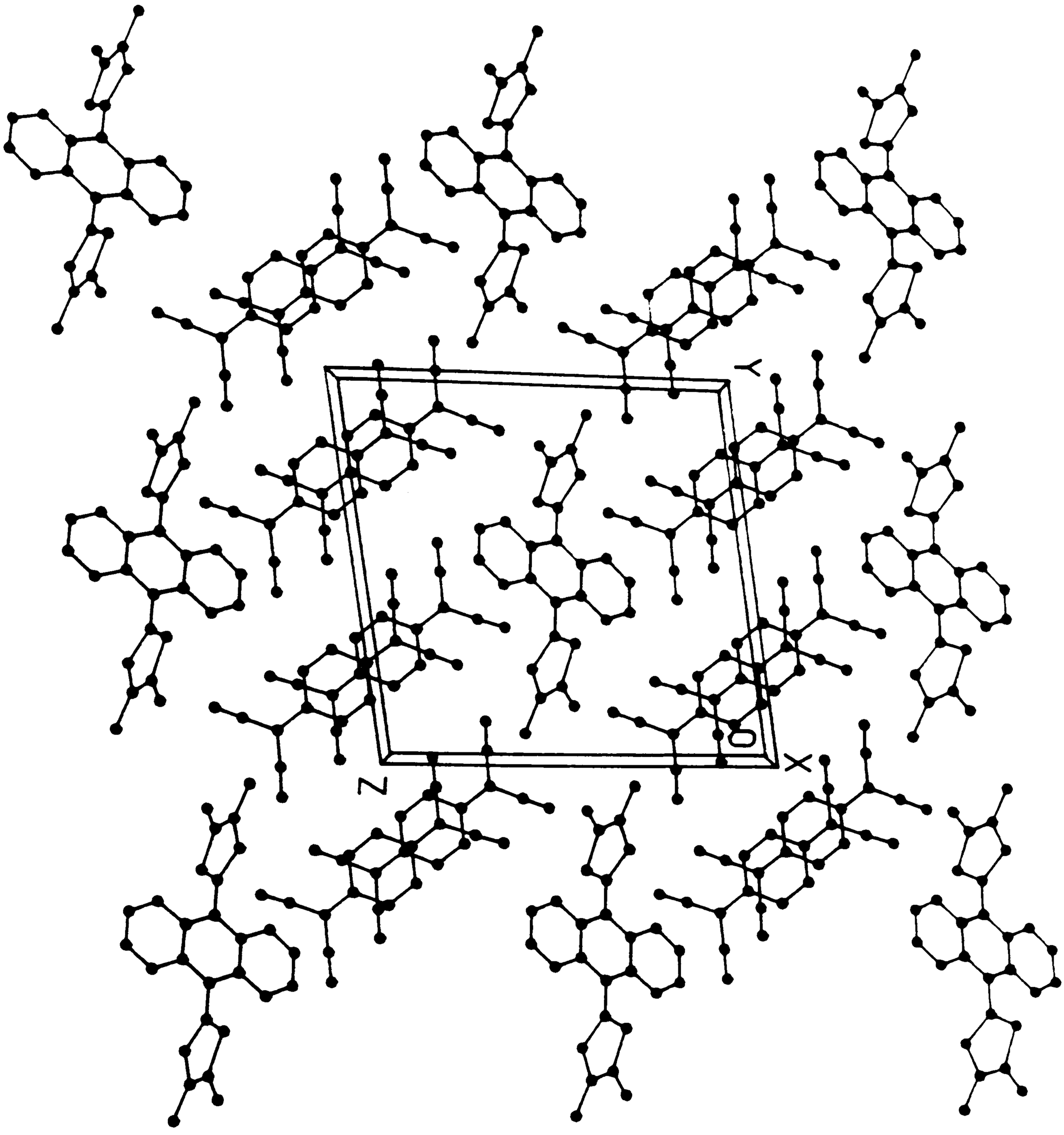


Figure 2.7: *X-Ray structure of complex (127a); view down a-axis.*

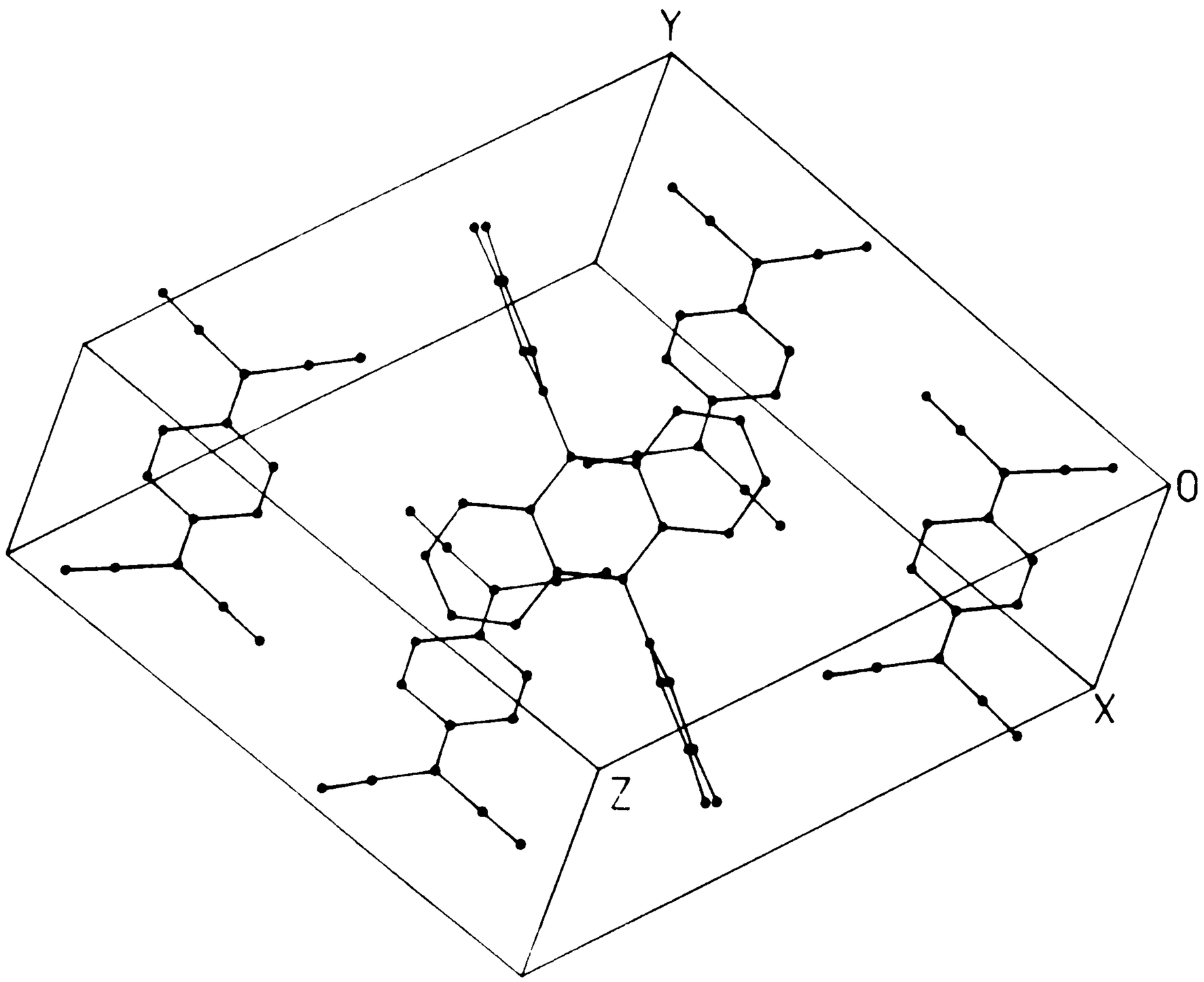


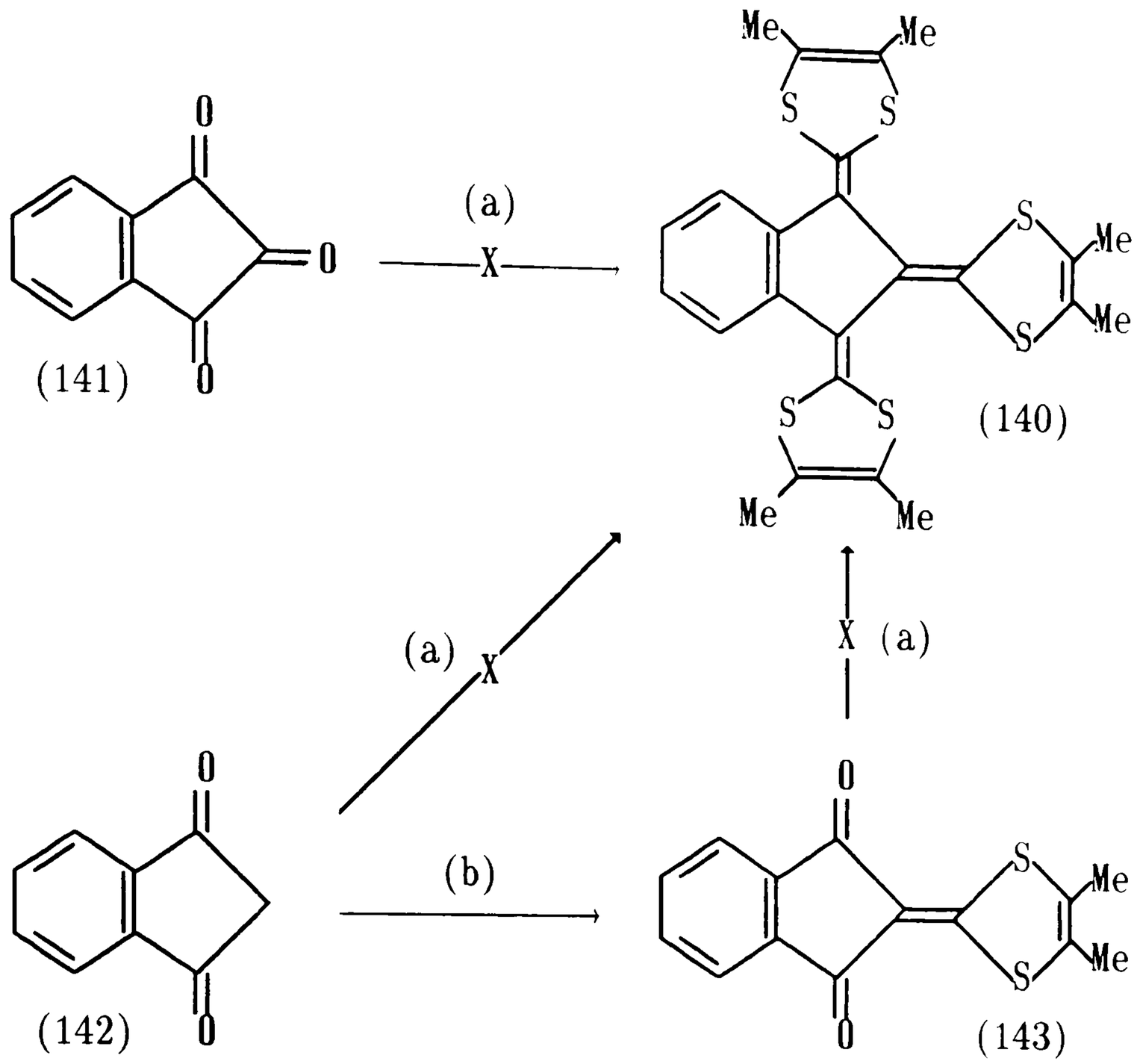
Figure 2.8: *X-Ray structure of complex (127a); view directly onto the plane of the anthracene ring.*

(Figure 2.2). The highly distorted structure of the neutral species (127) is dramatically different in the dication species in complex (127a). The anthracene rings are now perfectly planar and the 1.3-dithiole rings are orientated with their planes at 86^{o} to that of the anthracene ring (Figure 2.8). To our knowledge, such a marked change in the structure of a donor moiety on formation of a C-T complex is undocumented. The carbon-carbon bonds between the 1,3-dithiole rings and the anthracene portion of the dication are considerably longer in complex (127a) (1.487Å) than in the neutral donor (127) (1.362Å), consistent with the donor being present as the dication and the central rings having become aromatic.

In the light of this structure, it seems clear that the high conductivity observed in complex (127a) is associated with electron delocalisation along the highly-ordered TCNQ stacks. This study has emphasised, to an unprecedented extent, that planarity, or near planarity, in the donor is *not* a pre-requisite for the formation of an organic metal.

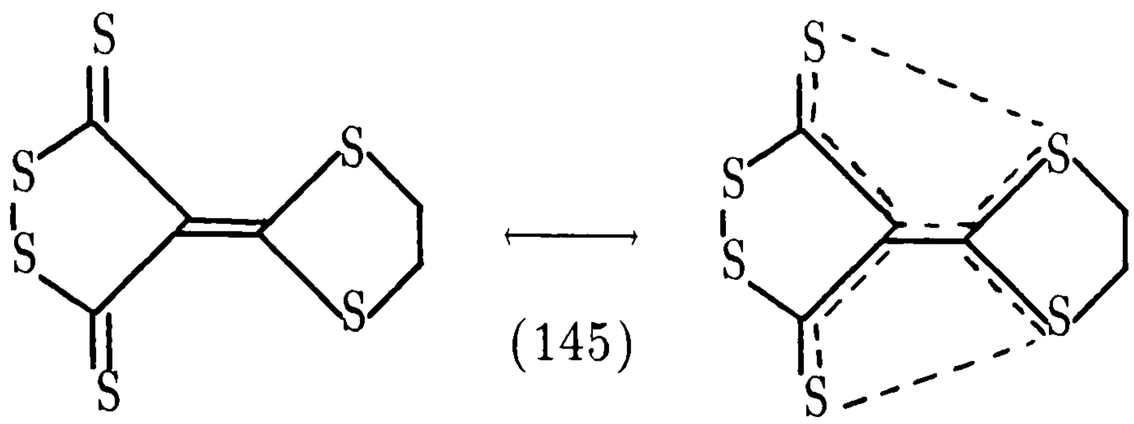
2.5 HETEROCYCLIC PRODUCTS DERIVED FROM 1,3-INDANDIONE

1,3-Dithiole-[n]-radialenes are of current interest as both multi-stage redox systems and promising donor components for the preparation of organic conductors and/or ferromagnets[77]. In the light of work published recently by Yoshida *et al.* on derivatives (54)-(56), we targeted our attentions at the unknown donor (140), the C-T complexes of which might display novel solid-state properties.



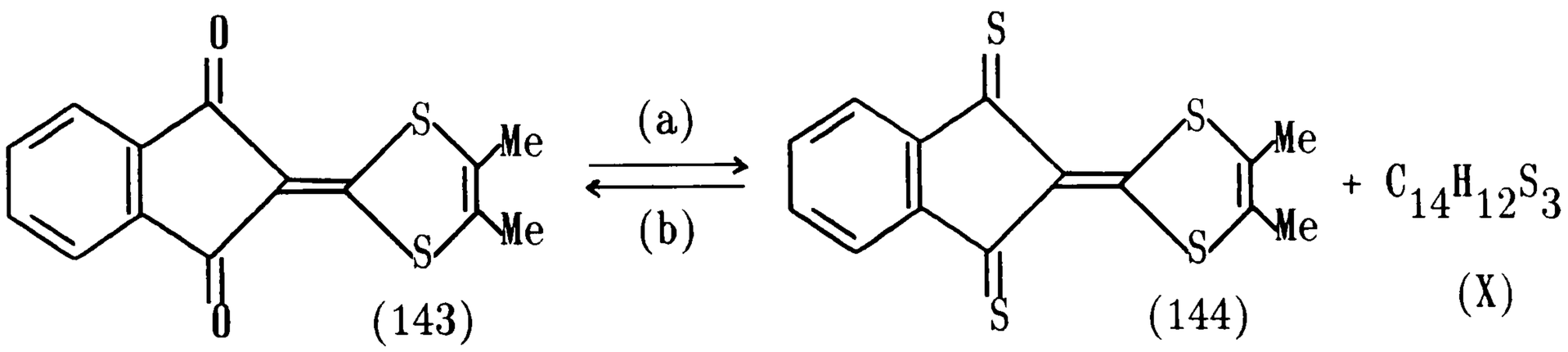
Scheme 2.18: *Reagents: (a) Reagent (121); (b) NaOMe, Reagent (116)*

Our initial stratagem was simply to treat 1,2,3-indantrione (141) with three equivalents of carbanion (121) under our standard conditions (Chapter 2.4.3); however, no reaction was observed. An alternative approach was to treat the anion of 1,3-indandione (142) with 2-methylthio-4,5-dimethyl-1,3-dithiolium iodide (116) in ethanol which gave the expected 1,3-dithiole-2-alkylidene product (143) in quantitative yield. Attempted reactions of compound (143) with one or two equivalents of carbanion (121) was unsuccessful and only starting materials were recovered. Initial Wittig-Horner reaction of 1,3-indandione (142) with carbanion (121) gave a complex mixture of products from which nothing could be isolated.



(145)

Compound (143) was, however, seen to be a promising precursor to compound (144), an analogue of the novel heteroaromatic trimethylene-methane (145) which has been shown to have unusual bonding participation by the sulphur atoms[139]. Reaction of (143) with either phosphorus pentasulphide or Lawesson's reagent as thionating agent in refluxing dry benzene, or toluene, gave compound (144). Although ^{13}C NMR data could not be obtained for compound (144), due to its insolubility in NMR solvents, the structure of (144) was supported by mass spectra, micro-analysis and by conversion back to compound (143) with mercuric(II) acetate (85% yield).

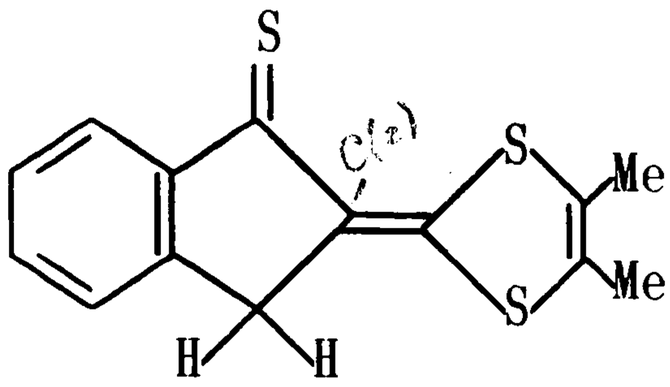


(143) (144) (X)

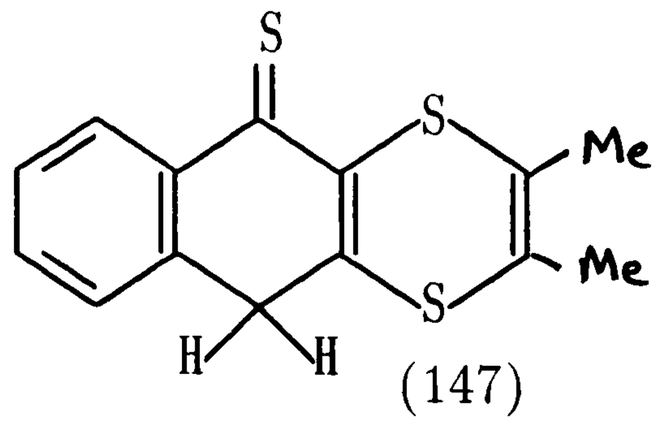
Scheme 2.19: *Reagents: (a) P_2S_5 or Lawesson's Reagent; (b) $Hg(OAc)_2$, HOAc*

We have also found an intriguing product (X) from thionation of the diketone (143), and by varying the reaction conditions this new product could be isolated in up to 80% yield. All analytical and spectroscopic data implied that product (X) was a single, pure compound with molecular formula $C_{14}H_{12}S_3$, fully consistent with one C=S group of (144) having been reduced to a methylene group. The CH_2 protons in product (X) are observed as a singlet at δ_H 3.79 ppm and the two methyl groups are clearly inequivalent (δ_H 2.28 and 2.24 ppm). The ^{13}C NMR spectrum seems

to discount structure (146), as the characteristic resonance of the C(2) carbon of a 1,3-dithiole-2-ylidene compound (expected at *ca.* 110 ppm)[140] is absent. This suggests that rearrangement of the 1,3-dithiole-2-ylidene system may have occurred. We have, therefore, considered other possible structures, isomeric with (146), for product (X), of which the novel 1,4-dithiin derivative (147) is consistent with the spectroscopic data. However, we have no evidence to confirm structure (147).



(146)



(147)

The formation of product (X) occurs equally well in benzene, or toluene, as solvent and no deuterium incorporation is observed in deuterated solvents. The best yields of product (X) (80%) were obtained when either the solvent was not dried or a small amount of water was added to "wet" the thionating agent. This may indicate that hydrogen sulphide plays an active role in the reaction course. However, attempts to reduce either diketone (143) or dithione (144) with hydrogen sulphide led only to recovery of starting material. To eliminate the possibility that product (X) was formed during reaction work-up, we treated dithione (144) with dilute base, basic alumina and silica; in all cases, these reagents failed to effect conversion of (144) to product (X). Clearly, further work is needed before the structure of product (X) can be assigned with confidence and the mechanism of its formation elucidated.

Cyclic voltammetry of compounds (143), (144) and (X) showed no oxidation in the limit of our experiments (1.15 V) indicating that they are all very poor donors. However, highly crystalline 1:1 complexes of (143) and (144) with TCNQ [(143a) and (144b) respectively] were obtained

in good yields on cooling warm solutions of (143),or (144), and TCNQ in dry acetonitrile. In agreement with the high oxidation potentials of compound (143) and (144), all data obtained for complexes (143a) and (144a) indicate that they are neutral complexes; that is, there is no intermolecular charge-transfer and the component molecules are present in their neutral states. The IR spectra of complexes (143a) and (144a) consist of sharp peaks typical of neutral, insulating complexes, and there is no apparent charge-transfer absorption. The cyanide absorptions of the TCNQ species in the complexes (143a) and (144a) are observed at 2200 cm^{-1}, which is diagnostic of neutral TCNQ[18]. Consistent with this, the complexes (143a) and (144a) are both electrical insulators ($\sigma_{rt} \sim 10^{-15}$ S cm^{-1}, two-probe, compaction measurement).

2.6 SUMMARY

New electron donors that are extended analogues of TTF have been prepared as both the dication and neutral species by efficient synthetic strategies. The suitability of these new extended donors in the field of organic conductors is established by the formation of conducting complexes with TCNQ. In particular, X-ray crystallography has revealed that the anthracenediylidene system adopts a very different conformation in the neutral and dication forms.

CHAPTER THREE

HIGHLY CONJUGATED SELENATRITHIAFULVALENE AND DISELENADITHIAFULVALENE DERIVATIVES: SYNTHESIS AND REACTIONS OF A NOVEL 1-SELENA-3-THIOLE WITTIG-HORNER REAGENT

3.1 INTRODUCTION

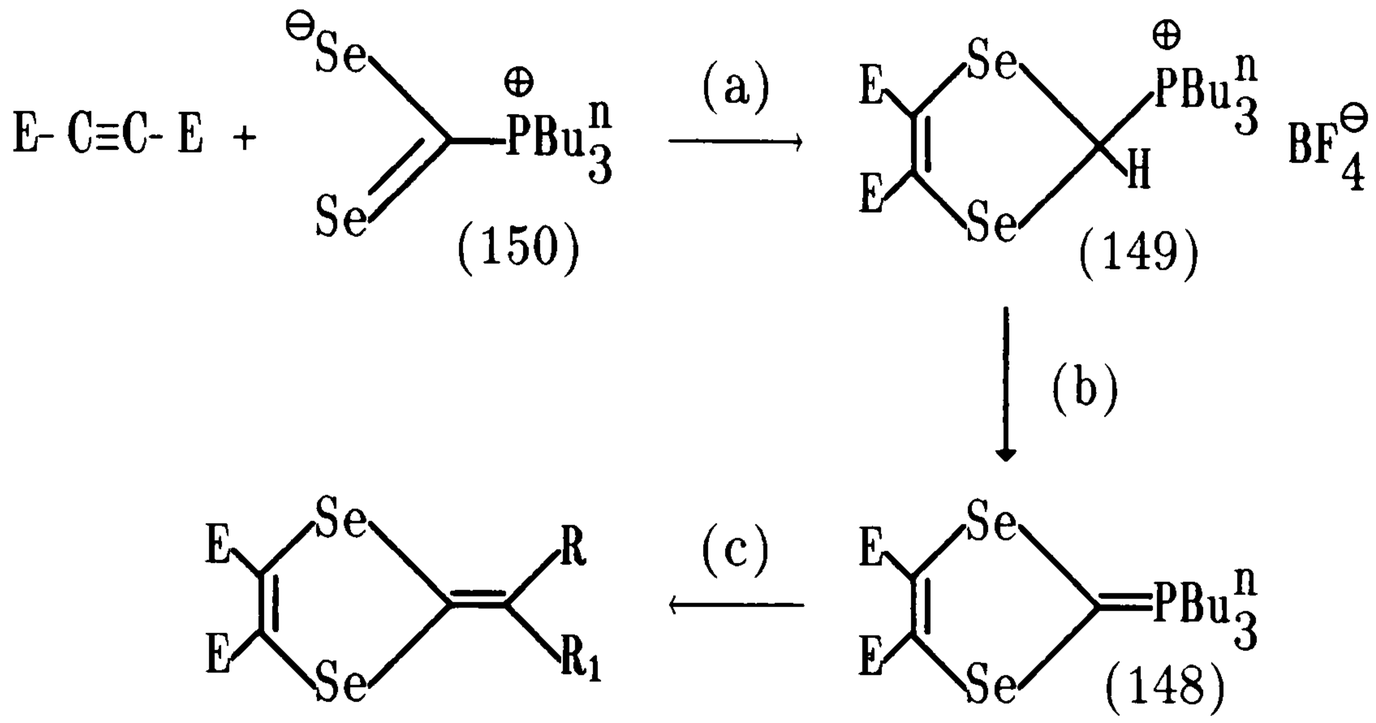
A primary goal in the field of organic metals is to understand the changes in the electrical and magnetic properties that accompany a systematic modification of the donor and acceptor moieties. Exciting discoveries have been realised by substitution of the sulphur atom in TTF with a larger chalcogen atom; this has proved to be one of the most effective ways to suppress the Peierls transition in low dimensional organic metals. For example, in the $(TMTSeF)_2X$ genre, the increased interchain interactions caused by close intermolecular Se··Se contacts play a crucial role in stabilising the superconducting state (Chapter 1.4.2). In general, the more diffuse 'p' and 'd' orbitals of the larger heteroatom give rise to increased interchain π-interactions in C-T complexes, leading to greater conduction bandwidths and thus, higher conductivities relative to their TTF analogues.

Several unsymmetrical TTF and TSeF derivatives have been prepared by cross-coupling methods, though these generally suffer the drawbacks of low yields and tedious chromatographic separation from a range of coupled products[20]. Notable among these compounds is the DMET donor (18), a hybrid molecule of TMTSeF (16) and ET (17), which forms superconducting ion-radical salts. A superconductor based on the all-sulphur asymmetric donor MDT-TTF (19) has also been described (Chapter 1.4.2).

3.1.1 Selenium Containing Phosphoranes

We were interested in extending our ylid methodology outlined in Chapter 2.4.3 to the synthesis of new unsymmetrical selenium-containing TTF analogues. The only known selenium-containing phosphorane based on

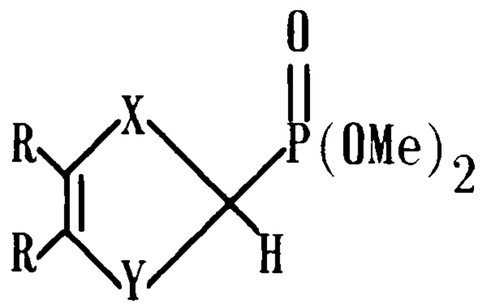
the 1,3-dithiole ring is ylid (148), which has been utilised in the efficient synthesis of diselenadithia- and tetraselena- vinylogues of TTF, (44) and (45) respectively[81]. The phosphonium salt (149) was prepared by 1,3-dipolar cycloaddition reaction of the tri-n-butyl-phosphine-carbon diselenide complex (150) with dimethylacetylene-dicarboxylate (DMAD) in the presence of tetrafluoroboric acid-diethyl-etherate (Scheme 3.1). Generation of the phosphorane (148) and subsequent Wittig reaction has been investigated by *in situ* reaction with a strong base and a ketone[81].



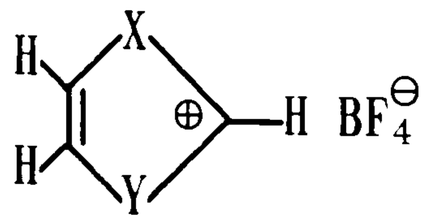
Scheme 3.1: *E = CO_2Me; Reagents: (a) $HBF_4.Et_2O$; (b) base; (c) $RR_1C=O$.*

This methodology, previously described by Cava *et al.* for the synthesis of the all-sulphur analogue (104, R = CO_2Me), is known to suffer the limitation of being applicable only to electron deficient acetylenes, and thus its synthetic application is limited[120].

In principle, a similar reaction procedure to that used for the synthesis of phosphonate esters (100) and (101) (Chapter 2.4.2) could provide the selenium-containing phosphonate esters (151) and (152), *ie.* treatment of the 1-selena-3-thiolium and 1,3-diselenolium cations, (153) and (154) respectively, with trimethylphosphite and sodium iodide in acetonitrile.



(100) X=Y=S; R=H
(101) X=Y=S; R=Me
(151) X=S; Y=Se; R=H
(152) X=Y=Se; R=H



(113) X=Y=S
(153) X=S; Y=Se
(154) X=Y=Se

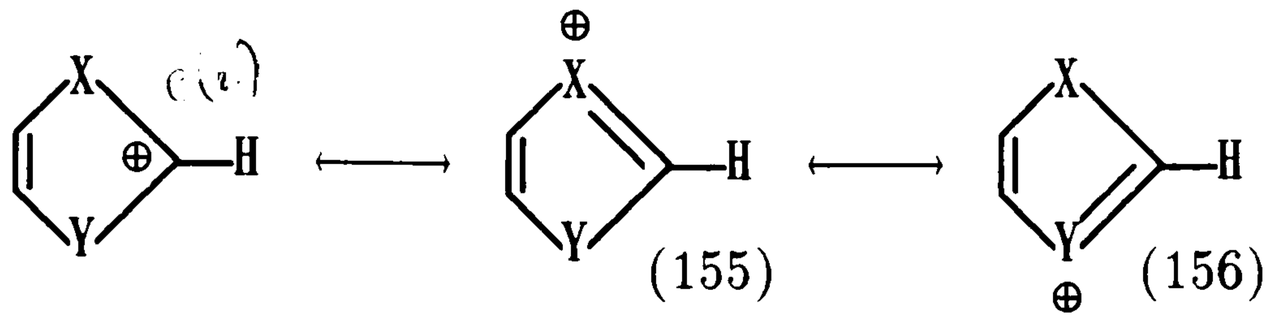
3.1.2 NMR Investigation of Cations (113), (153) and (154)

NMR investigation of the 1,3-dithiolium (113), 1-selena-3-thiolium (153) and 1,3-diselenolium (154) cations has shown a displacement to lower field of the methine protons, consistent with a change in the charge density distribution upon progressive selenium substitution (Table 3.1)[141].

PROTONS δ_H (ppm)	CATION (113)	(153)	(154)
Methine	11.43	12.43	13.41
Vinyl	9.45	9.48 10.18 AB, J=6Hz	10.22

Table 3.1: *^1H NMR Chemical shift data for cations (113), (153) and (154), solvent CF_3COOH.*

The data indicate that more positive charge is located on C(2) upon selenium substitution. It is well-known that selenium enters into π-bonding with carbon less efficiently than sulphur[142]; this means that resonance stabilising canonical forms, *eg.* (155) and (156), should contribute less when X and/or Y = Se, than when X and Y = S.



(155) (156)

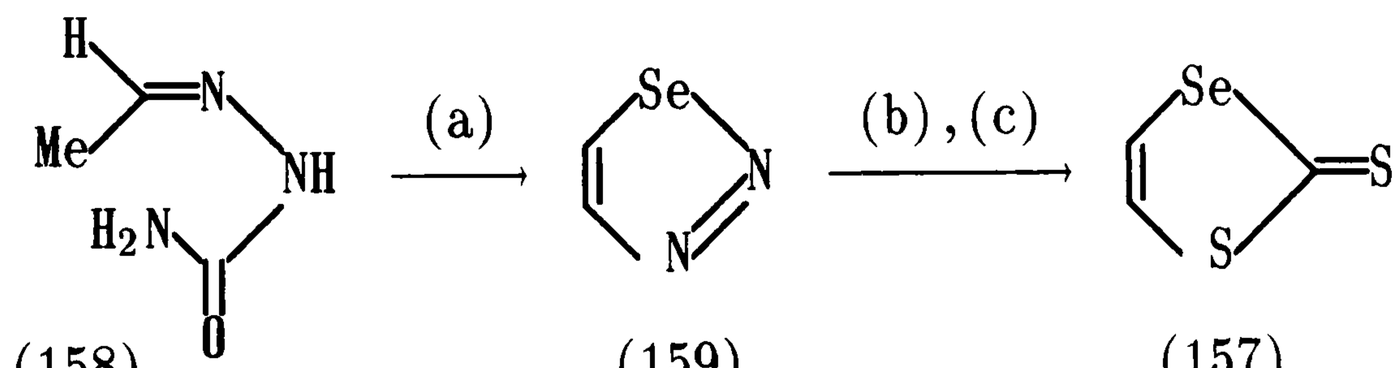
Consistent with this, the cations (153) and (154) have been reported to be less stable than cation (113)[141]. Indeed, the failure of triethylamine-induced coupling of the 1,3-diselenolium cation (154) to yield TSeF has been attributed to the extreme instability of cation (154)[143]. This fact, together with the cost and extreme toxicity of carbon diselenide, the precursor to cation (154), has meant the chemistry of phosphonate ester (152) was not investigated.

The 1-selena-3-thiolium cation (153) has, however, been reported to be relatively easy to handle; we, therefore, chose to investigate the ylid derived from the phosphonate ester (151) as a new precursor to introduce selenium into the TTF skeleton.

3.2 SYNTHESIS AND REACTIONS OF THE NOVEL WITTIG-HORNER REAGENT (151)

3.2.1 Preparation of Phosphonate Ester (151)

1-Selena-3-thiole-2-thione (157) was prepared using a route outlined by Cava *et al.* without significant modification (Scheme 3.2)[144].

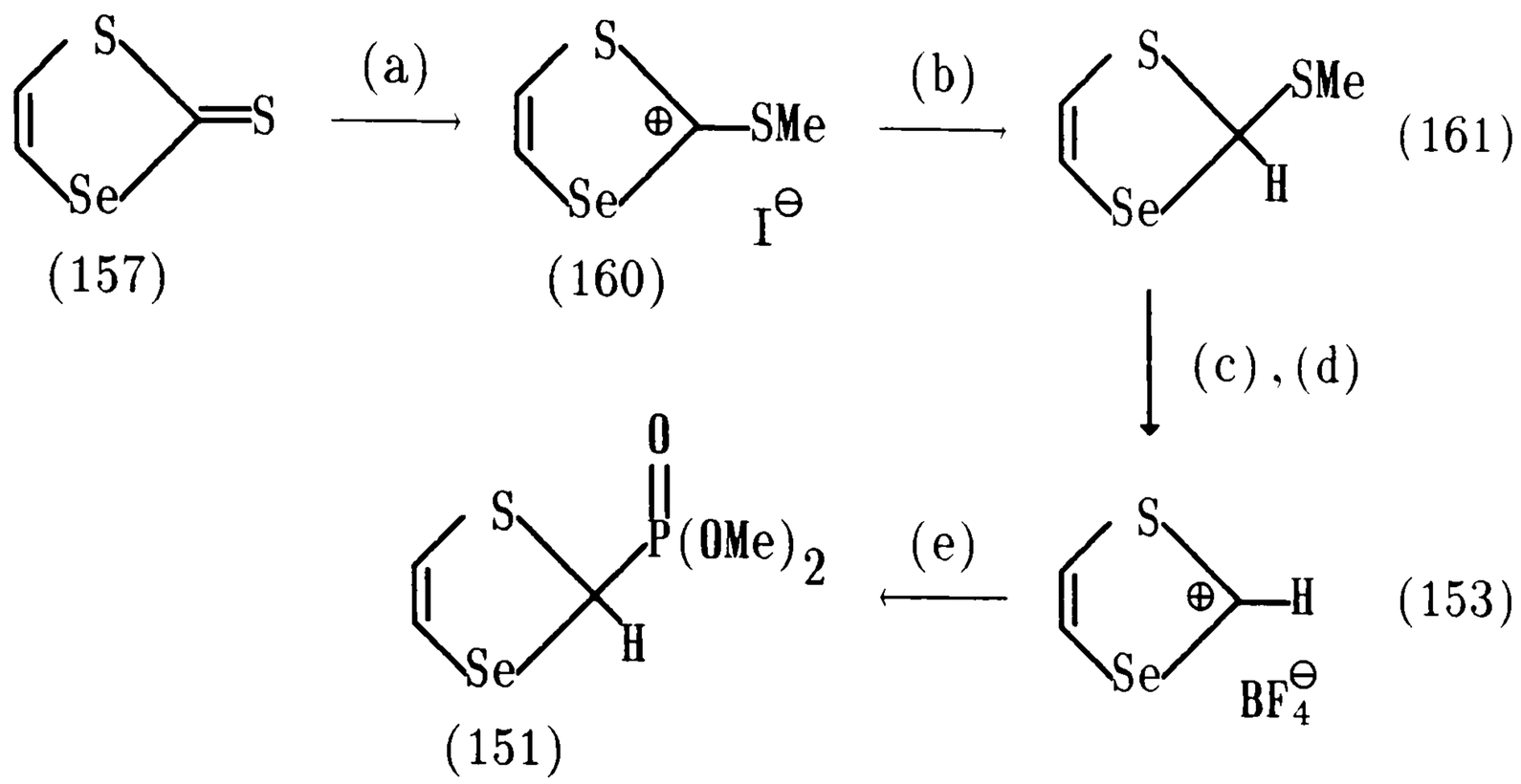


(158) (159) (157)

Scheme 3.2: *Reagents: (a) SeO_2; (b) t-BuOH/DMF/CS_2; (c) HCl.*

Thus, treatment of acetaldehyde semicarbazone (158) with selenium dioxide in a two-phase system with a phase transfer catalyst gave 1,2,3-selenadiazole (159); addition of potassium t-butoxide to a solution of (159) in t-butanol/DMF and excess carbon disulphide gave thione (157). The 1-selena-3-thiolium cation (153) was easily prepared from thione

(157) in a clean, high-yielding three-step procedure (Scheme 3.3)[141,144] analogous to the routes outlined for the preparation of cations (113) and (114) (Chapter 2.4.2).



Scheme 3.3: *Reagents: (a) MeI; (b) $NaBH_4$; (c) AcOAc; (d) $HBF_4.Et_2O$; (e) $(MeO)_3P$, NaI.*

Alkylation of thione (157) at 50°C with methyl iodide in nitromethane precipitated the methiodide salt (160) (95% yield), which was conveniently reduced with sodium borohydride in ethanol at room temperature to give compound (161) as a hygroscopic oil (90% yield); treatment of (161) with acetic anhydride followed by tetrafluoroboric acid-diethyletherate afforded the cation (153) (90% yield) as a white solid. The cation (153) decomposed slowly on standing at -20°C under nitrogen and was always used within four weeks of preparation. It is notable that peracid oxidation of 1-selena-3-thiole-2-thione (157) fails to yield cation (153); instead, it appears that selenium oxidation occurs[145]. The phosphonate ester (151) was cleanly isolated as a hydrolytically unstable red oil by Michaelis-Arbuzov reaction of cation (153) with freshly-distilled trimethylphosphite and sodium iodide in dry acetonitrile at room temperature (90% yield). The ester (151) was purified by dry column chromatography but could not be purified sufficiently for satisfactory elemental analysis. The ester was identified by ^1H NMR,

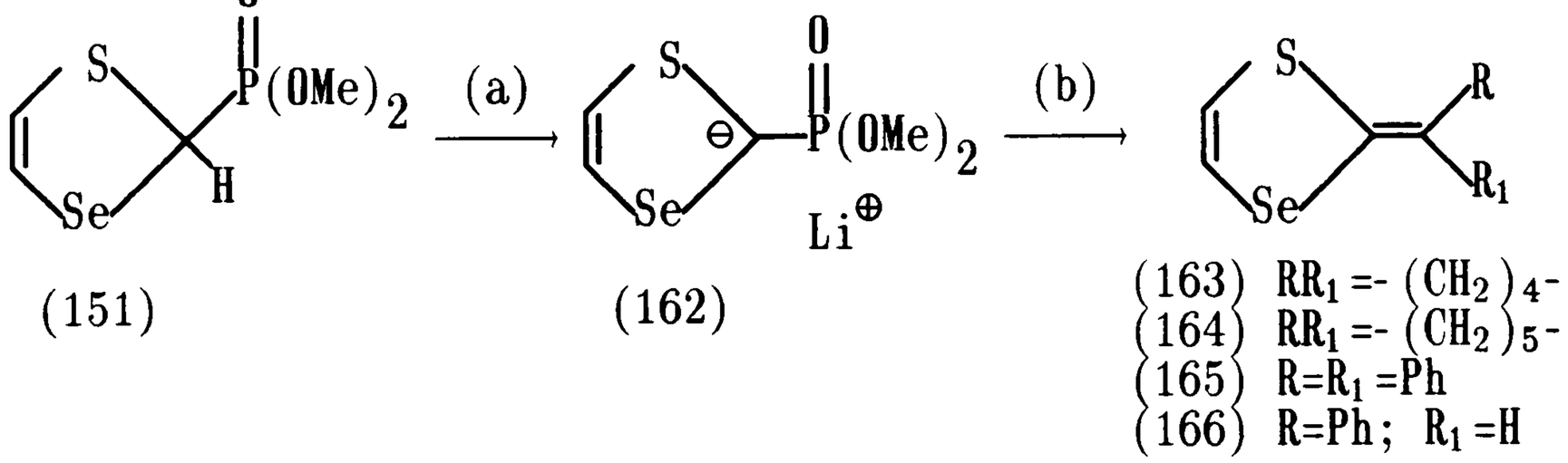
infrared and mass-spectral evidence (Table 3.2). The instability of ester (151) meant it was best used in subsequent reactions immediately after isolation.

IR (cm^{-1})	1240 (P=O); 1020-1050 br (P-O-C)
MS[a] [Intensity%]	260 [20,M^+]; 163 [100,M^+-P(=O)(OMe)$_2$]
^{1}H NMR (ppm)	6.67 and 6.43 (each 1H,AB J=8 Hz) 5.26 (1H,d,J=4.5 Hz) 3.31 (6H,d,J=10 Hz)

Table 3.2: *Physical data for phosphonate ester (151); (a) Based on ^{80}Se isotope.*

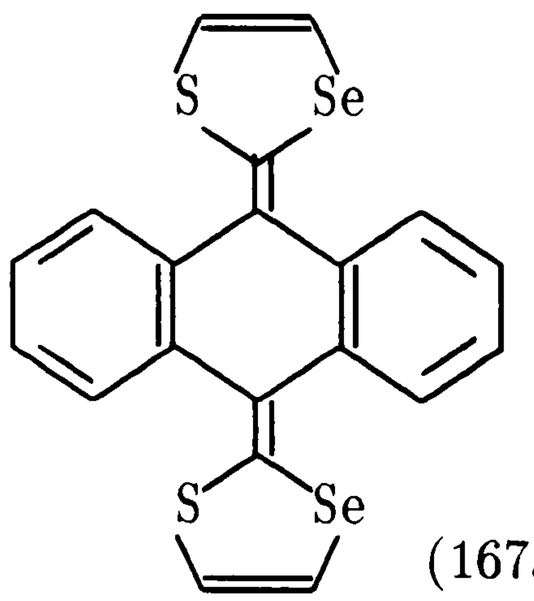
3.2.2 Wittig-Horner Reaction of Phosphonate Ester (151)

The phosphonate ester (151) was found to be readily deprotonated with n-butyllithium in THF at -78^{o}C; a concomitant colour change was observed in solution. The phosphonate carbanion (162) formed was trapped by addition of a variety of carbonyl compounds at -78^{o}C, and subsequent warming of the mixture to room temperature. For example, Wittig-Horner reaction of carbanion (162) with cyclopentanone, cyclohexanone, benzophenone and benzaldehyde gave compounds (163), (164), (165) and (166), respectively, with yields between 60 and 75% after purification. These products were identified by elemental analysis, ^{1}H NMR and mass spectra.

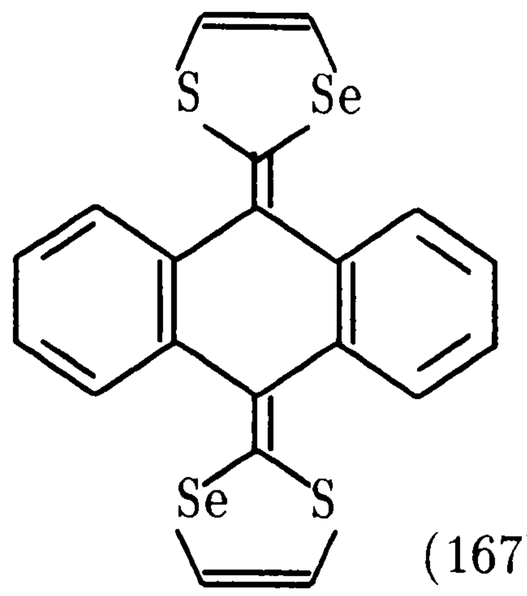


Scheme 3.4: *Reagents: (a) n-BuLi, -78^{o}C; (b) RR_1C=O.*

Having developed the novel mixed sulphur-selenium Wittig-Horner reagent (151), we were keen to investigate its reactions with anthraquinone with a view to forming novel extended donors. Treatment of two equivalents of the carbanion (162) in THF at -78°C with a suspension of anthraquinone in THF gave, after work-up and purification. the diselenadithiafulvalene derivative (167) as an orange, air-stable solid (*ca.* 60% yield).



(167a)

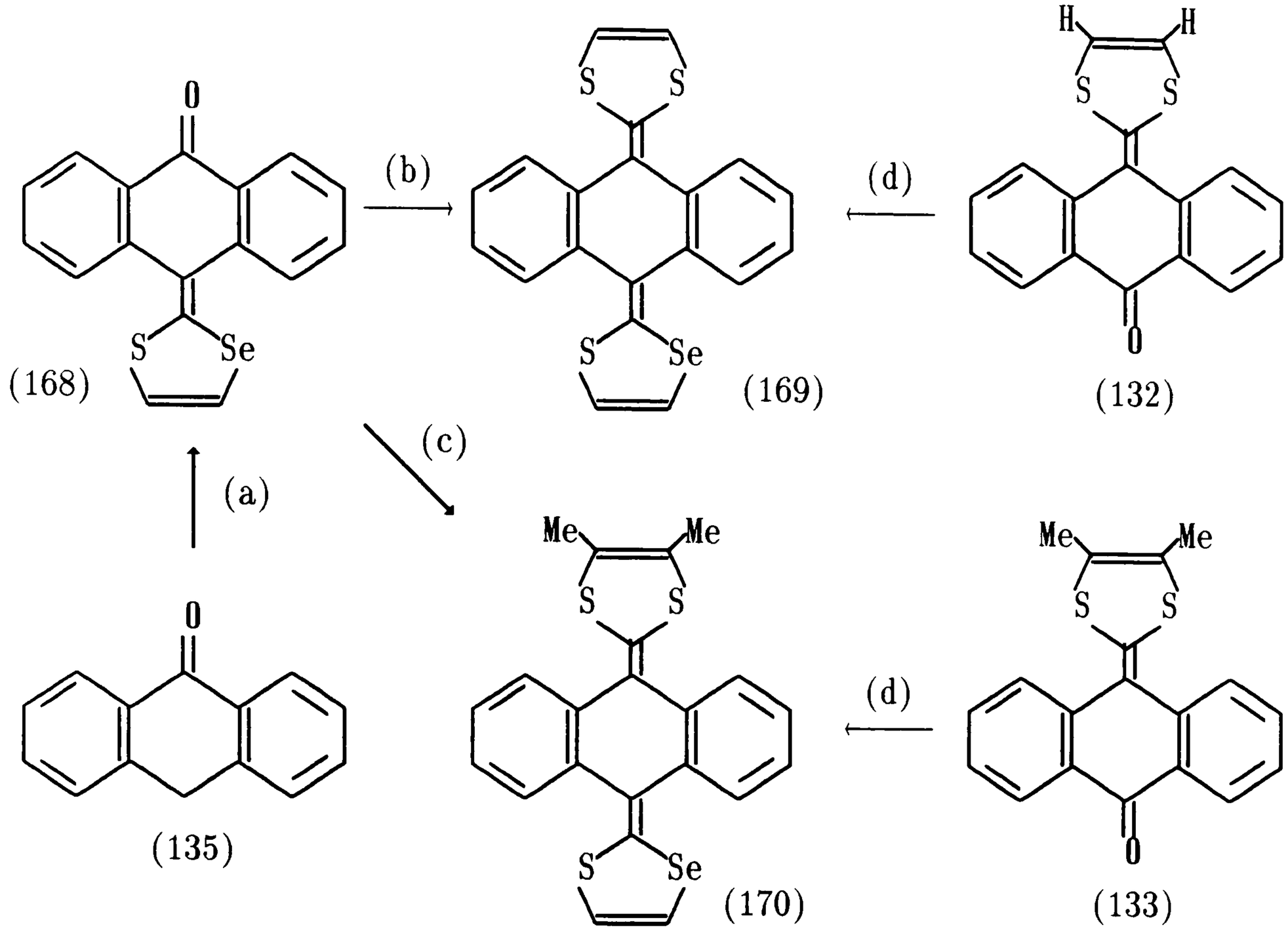


(167b)

The product exhibited two distinct AB coupling patterns for the 4,5-protons in the ^{1}H NMR, having approximately equal integrals indicating a 50:50 mixture of geometrical isomers [*cis* (167a) and *trans* (167b)] [*cf.* DSeTTF (14) is also isolated as an inseparable mixture of geometrical isomers[145]]. The protons resonating at low field are assignable to those adjacent to the sulphur atom[141]. The isomers (167a) and (167b) could not be distinguished by TLC. They appear to be thermally stable, as their NMR signals do not coalesce on heating to 85°C and there is no change in the NMR spectrum after heating at 150°C in DMSO for 10 hours.

The crude reaction mixture was also found to contain the mono-substituted anthraquinone (168) in about 10% yield; ketone (168) was, however, better obtained by treatment of one equivalent of carbanion (162) with anthraquinone under identical reaction conditions, yields being typically 50% after a difficult and tedious chromatographic separation from unreacted anthraquinone. Alternatively, utilising our

previous methodology (Chapter 2.4.3), ketone (168) was prepared in excellent yields (86%) by reaction of anthrone (135) in refluxing pyridine/acetic acid with the mixed sulphur-selenium methiodide (160). Reaction of ketone (168) with carbanion (162) gave compound (167) in 75% yield as a mixture of *cis/trans* isomers.



Scheme 3.5: *Reagents: (a) reagent (160); (b) carbanion (120); (c) carbanion (121); (d) carbanion (162).*

The unsymmetrical selenatrithiafulvalene extended donor system was accessed by simple reaction of ketones (132) and (133) with carbanion (162), giving donors (169) and (170), respectively, as orange air-stable solids (yields *ca.* 65%) (Scheme 3.5). Alternatively, the same products could be prepared by reacting one equivalent of carbanions (120) and (121) with ketone (168). Extended donors (169) and (170) are especially notable as they are the first analogues of the selenatrithiafulvalene system to be characterised.

3.3 CYCLIC VOLTAMMETRY OF DONORS (167), (169) AND (170)

The donor ability of a TTF derivative is gradually reduced by incorporation of selenium into the ring system (Table 3.3)[146].

COMPOUND		E_1	E_2
TTF	(2)	0.34	0.71
DSeTTF	(14)	0.40	0.72
TSeF	(9)	0.48	0.76

Table 3.3: *CV data for compounds (2), (9) and (14); vs Ag/AgCl, Pt button electrode, scan rate = 200 mV sec^{-1}; 5 x 10^{-5} M donor, 0.1 M $[Bu_4N][ClO_4]$ in MeCN; see ref. 146.*

This is attributable to selenium forming weaker π-bonds with carbon than does sulphur. Thus, the selenium-containing cations are less stable than their sulphur counterparts, as the former are less able to redistribute charge: this raises the overall energy required for ionisation as selenium is substituted for sulphur. This phenomenon is quite clearly observed with the extended anthraquinone ring system (Table 3.4).

COMPOUND	E_{ox}	E_{red}
(167)	0.51	-0.02
(169)	0.47	0.11
(170)	0.45	0.09
(127)	0.42	0.07
(126)	0.40	0.20

Table 3.4: *CV data for extended anthraquinone donors; vs Ag/AgCl, Pt button electrode, scan rate = 100 mV sec^{-1}; 5 x 10^{-5} M donor, 0.1M $[Bu_4N][ClO_4]$ in MeCN.*

In all cases, one two-electron redox couple is observed by cyclic voltammetry, although the process does not appear to be cleanly reversible (Figure 3.1) (see Chapter 2.4.6).

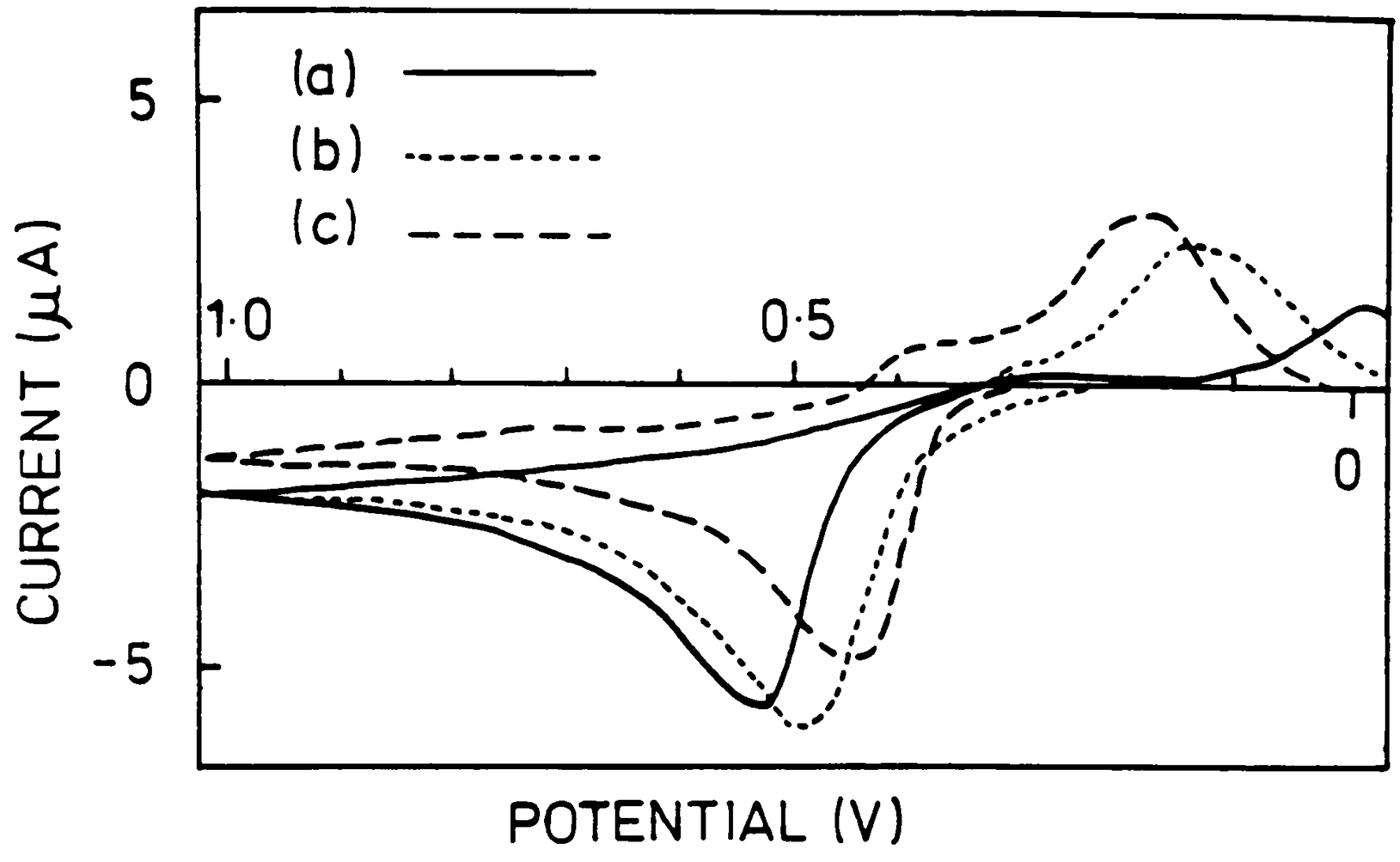


Figure 3.1: *Cyclic voltammograms of (a) donor (167); (b) donor (169) and (c) donor (126).*

The donors (167), (169) and (170) are poorer donors than TTF when E_1 values are considered, although in all cases the second electron is donated more readily; this behaviour has precedent in other donors with extended conjugation[65,68,70,73]. Similarly, there is an increase in the ionisation potential of ketone (168) relative to ketone (132) after selenium incorporation with a single, reversible one-electron redox couple observed at $E_1^{\frac{1}{2}}$ = 0.90 V (Figure 3.2) [*cf.* ketone (132), $E_1^{\frac{1}{2}}$ = 0.85 V].

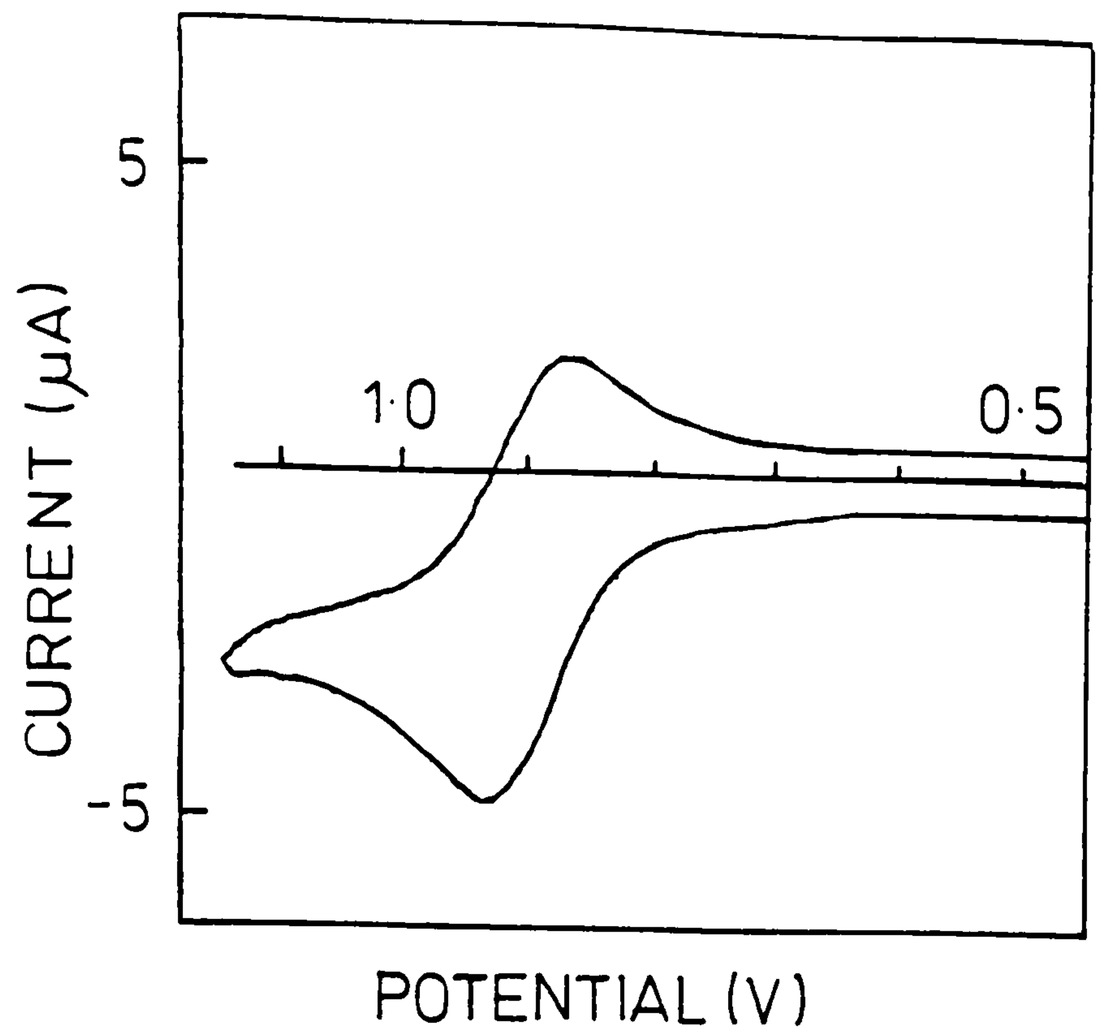


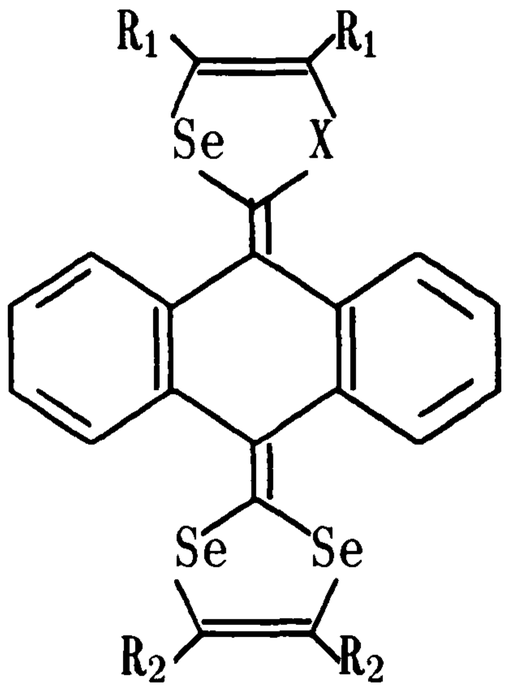
Figure 3.2: *Cyclic voltammogram of ketone (168).*

3.4 C-T COMPLEXES OF DONORS (167), (169) AND (170)

The donors (167), (169) and (170) all form C-T complexes when boiling solutions of donor and TCNQ in dry acetonitrile are mixed together, as indicated by the immediate formation of a dark green-blue solution. Furthermore, charge-transfer from donor to TCNQ was confirmed by the appearance of the characteristic solution-state UV absorptions of the TCNQ radical-anion (840, 760 and 390 nm)[133]. However, on cooling solutions obtained from a variety of donor : TCNQ stoichiometries, amorphous black powders of irreproducible elemental analyses were isolated. It is possible that a number of different complexes of varying stoichiometry form simultaneously, as is known to occur in a number of other donor-acceptor systems[147]. Elemental analysis was indicative of a donor : TCNQ stoichiometry of between 1:2 and 1:4 and preliminary conductivity measurements show these complexes to be semi-conducting ($\sigma_{rt} \sim 1 \times 10^{-3}$ S cm^{-1}, two probe, compaction measurement).

3.5 FUTURE WORK

Further members of the series of extended donors derived from anthraquinone, *viz.* the tri- and tetra-selena systems, (171) and (172) respectively, have not been reported. The use of phosphorane (148) described by Yoshida *et al.*[81] could provide compounds (173) and (174), and subsequent decarbomethoxylation using $LiBr.H_2O$ in HMPA[148] should yield the parent donors (171) and (172). The diselenaphosphonate ester (152) is, as yet, unknown.



(171) X=S; $R_1=R_2=H$
(172) X=Se; $R_1=R_2=H$
(173) X=S; $R_1=H$; $R_2=CO_2Me$
(174) X=Se; $R_1=R_2=CO_2Me$

3.6 CONCLUSIONS

In conclusion, we have extended our methodology outlined in Chapter 2.4 to establish a high-yielding synthetic route to the novel 2-dimethoxyphosphinyl-1-selena-3-thiole (151), which serves as a versatile precursor for synthesising mixed, extended sulphur-selenium donors. Carbanion (162) has been trapped cleanly to yield the first reported selenatrithiafulvalene derivatives (169) and (170).

CHAPTER FOUR

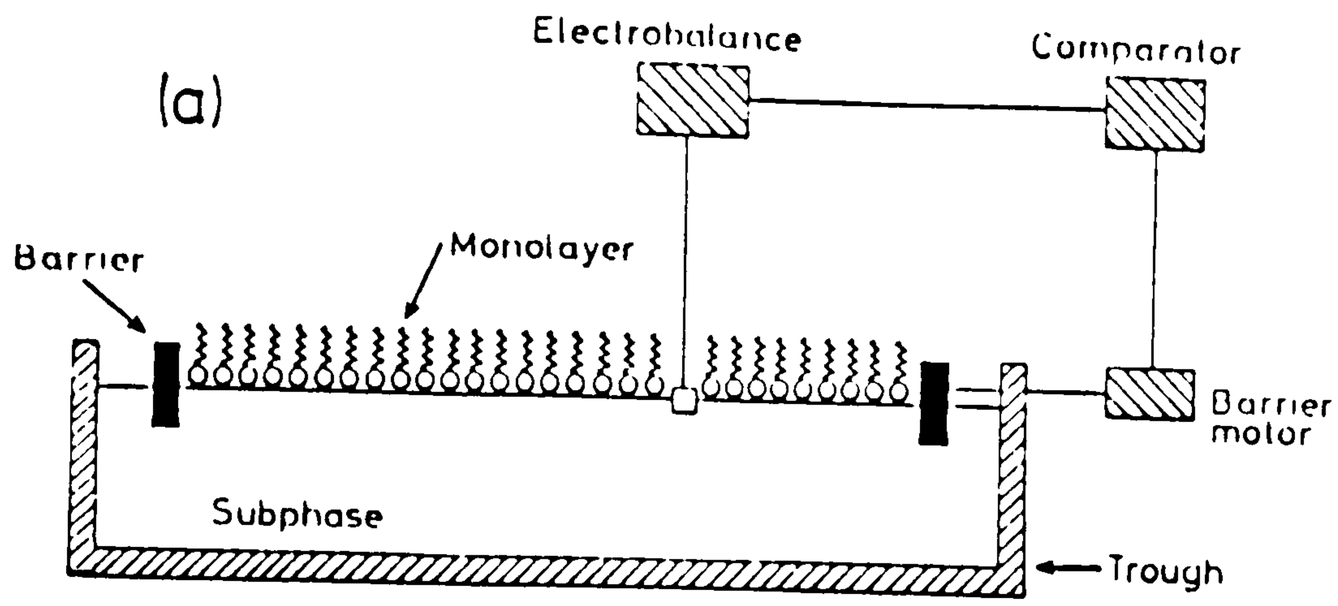
SYNTHESIS OF MONO-SUBSTITUTED TTF DERIVATIVES - ELECTROACTIVE LANGMUIR-BLODGETT FILMS OF TTF ESTERS AND THIOESTERS

4.1 INTRODUCTION

The Langmuir-Blodgett (LB) technique enables the fabrication of ultra-thin films with controlled thickness and regular arrangement of molecules[91]. Compounds suited for LB film formation are primarily the classical amphiphiles consisting of hydrophilic head groups and long-chain hydrophobic substituents[149]. However, molecules of completely different structures such as phthalocyanines[150], porphyrins[151], oligo-thiophenes[152] and quinones[153] have also been reported to form stable LB films. Highly-ordered organic ultra-thin films have already been extensively studied in many areas of electronics research, such as non-linear optics, pyroelectrics and sensing. However, very recently, electroactive LB films of C-T complexes have become the focus of keen attention (Chapter 1.4.4).

4.1.1 The LB Technique

LB films are prepared by spreading a small quantity of an amphiphilic material, dissolved in a volatile solvent (*eg.* chloroform), onto the surface of ultra-pure water (the subphase). A schematic diagram of the experimental arrangement for the deposition of LB films is shown in Figure 4.1(a). When the solvent has evaporated, the organic molecules are laterally compressed to form a compact mono-molecular film at the air-water interface [Figure 4.1(b)]. Interaction of the hydro-phobic and hydrophilic parts of the molecules ensures that, during compression, the individual molecules are aligned in the same way. Monolayers may then be conveniently removed from the water surface by dipping and raising a suitably prepared solid plate (the substrate) through the monolayer-air interface. Careful control of the surface



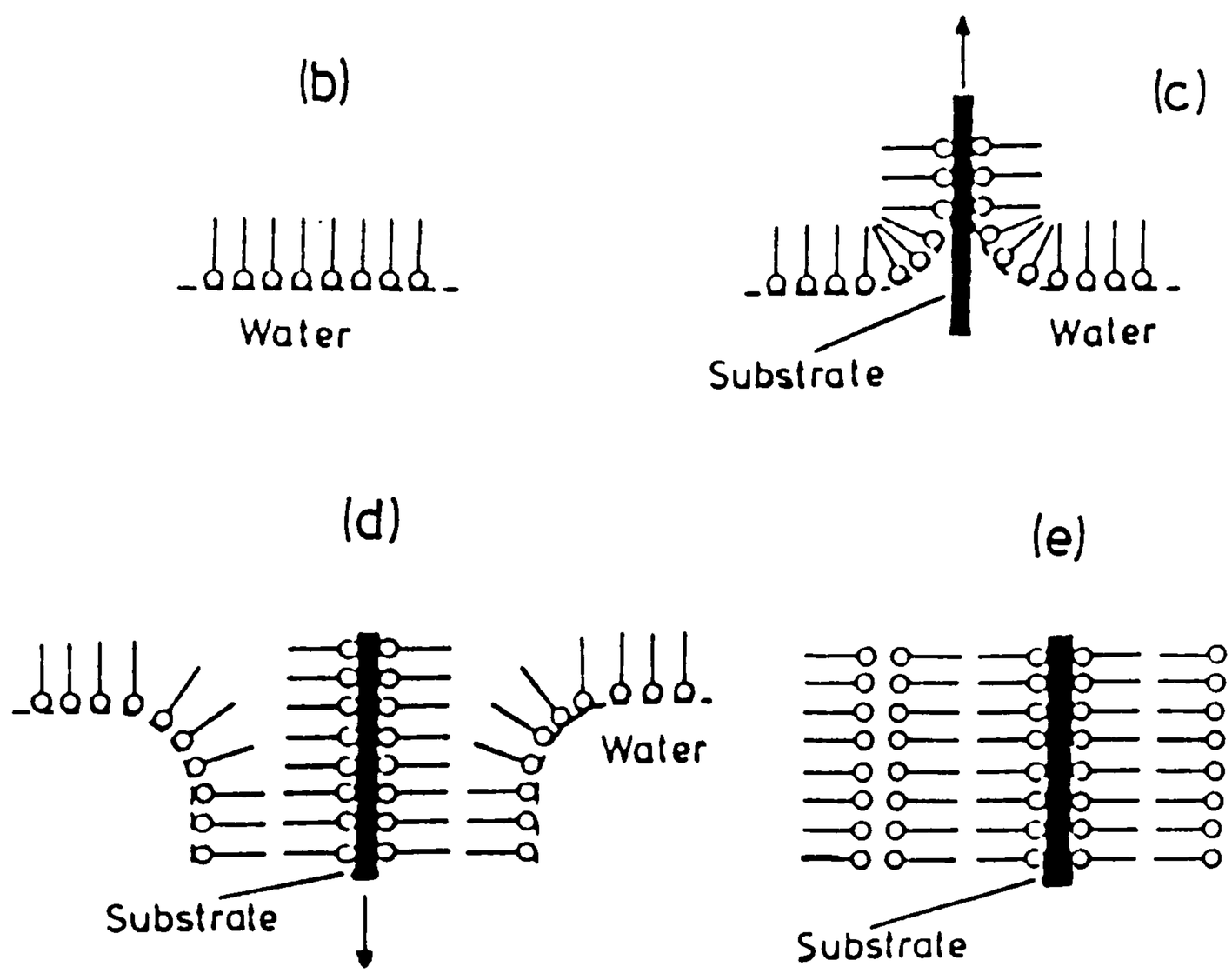


Figure 4.1: *Langmuir-Blodgett film deposition; (a) schematic diagram of a Langmuir trough; (b) mono-molecular film at air-water interface; (c) first withdrawal of substrate; (d) second immersion of substrate; (e) a Y-type film.*

pressure of the monolayer is required during this process. With a hydrophilic substrate no pick-up occurs during the first immersion: the first monolayer is deposited during the first withdrawal [Figure 4.1(c)]. Thereafter, a number of deposition modes are possible: for the most common "Y-type" deposition, a monolayer is transferred from the water surface on both the inward and outward movements of the substrate [Figure 4.1(d)]. As shown in Figure 4.1(e), these stack in a head-to-head and tail-to-tail configuration. "X-type" and "Z-type" depositions are also possible, referring to situations where the monolayer is deposited only as the substrate is lowered into the subphase, or only as it is being raised, respectively. The LB technique is, therefore, an elegant method of building up organic films of regular orientation, with an accurate control of thickness.

4.1.2 Donor Molecules Suitable for LB Film Formation

Traditionally, most conducting C-T complexes are characterised as single crystals or microcrystalline powders. However, the LB technique is becoming established as an alternative method of assembling highly ordered arrays of donor and/or acceptor molecules (Chapter 1.4.4).

Extending the work begun in our laboratory on alkanoyl-TTF's (71)[105], we have now sought to synthesise new mono-substituted TTF derivatives with various hydrophobic side-chains suitable for LB film formation. Work from Bechgaard's laboratory has highlighted the fact that any hydrophilic functionality in the side-chain must be located near the TTF ring if high quality conducting films are to be realised[104]. Our targets are, therefore, monofunctionalised TTF derivatives with alkyl groups attached directly to the TTF ring, or attached through ester, thioester or thioketone functionality.

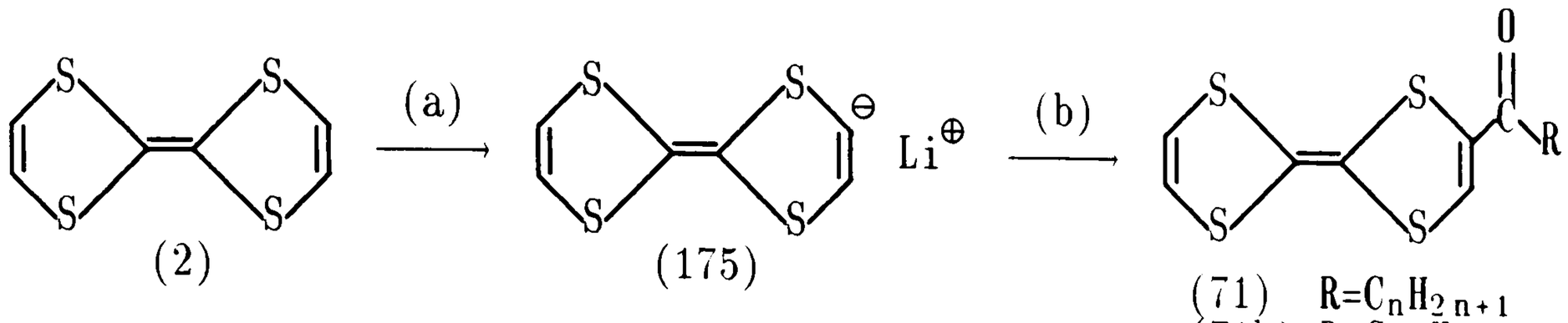
4.1.3 Synthesis of Mono-substituted TTF Derivatives

Symmetrically di- and tetra- substituted derivatives of TTF are generally prepared by coupling reactions of substituted 1,3-dithiolium cations or, more often, substituted 1,3-dithiole-2-ones, thiones or selenones (Scheme 2.1). Unsymmetrically substituted derivatives, though, are more difficult to obtain *via* this coupling technique, as symmetrically substituted derivatives are equally likely to form during reaction, presenting the often formidable task of separation. An alternative efficient route to monosubstituted TTF's was extensively investigated by Green in the late 1970's[154]. TTF is readily metallated to form the monolithio- derivative (175) by treatment with one equivalent of LDA in dry ether at -78°C. Subsequent reaction of anion (175) with electrophiles at -78°C, followed by warming to room temperature overnight, gave monofunctionalised-TTF derivatives in moderate yields (typically 25-50%). Substituents attached by this method include CH_3, CO_2H, C(=O)Me and CH_2OH groups. The direct reaction of TTF with electrophiles leads to oxidation to the radical cation, or dication, salts of TTF rather than substitution[14,155].

4.2 SYNTHESIS OF NEW MONO-SUBSTITUTED TTF DERIVATIVES

In our laboratory we have synthesised alkanoyl-TTF derivatives (71) in a convenient one-pot procedure from monolithio-TTF (175) and the appropriate acyl chloride (Scheme 4.1)[105]. Although compounds (71) form films of excellent quality, the donor ability of the molecule is quite significantly reduced relative to TTF by the presence of the electron withdrawing carbonyl group [*cf.* TTF: $E_1^{\frac{1}{2}} = 0.34$, $E_2^{\frac{1}{2}} = 0.71$; (71b): $E_1^{\frac{1}{2}} = 0.53$, $E_2^{\frac{1}{2}} = 0.92$ V]. It is known that the ionisation potential of TTF

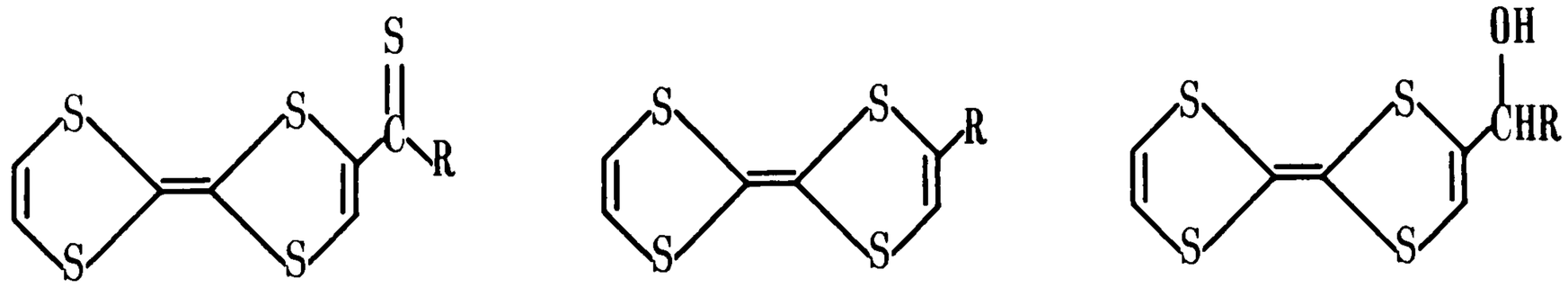
systems plays a key role in determining properties of crystalline C-T complexes[2a], so we initially sought to reduce the ionisation potential of donor (71b) by converting the carbonyl group to both thiocarbonyl and methylene groups.



Scheme 4.1: *Reagents: (a) LDA; (b) RCOCl.*

4.2.1 Synthesis of Thioketone (176)

Reaction of 1 equivalent of (71b) with 0.6 equivalents of Lawesson's reagent in refluxing dry benzene, or toluene, gave compound (176) (50% yield) as a dark blue solid. The product was identified by high resolution mass spectral evidence and the absence of a carbonyl absorption in the IR spectrum, but could not be obtained analytically pure. It is noteworthy that analogous reaction of (71b) with phosphorus pentasulphide gave poorer yields of (176) (< 30%). Investigation of the LB films of compound (176) has not been undertaken.[1]

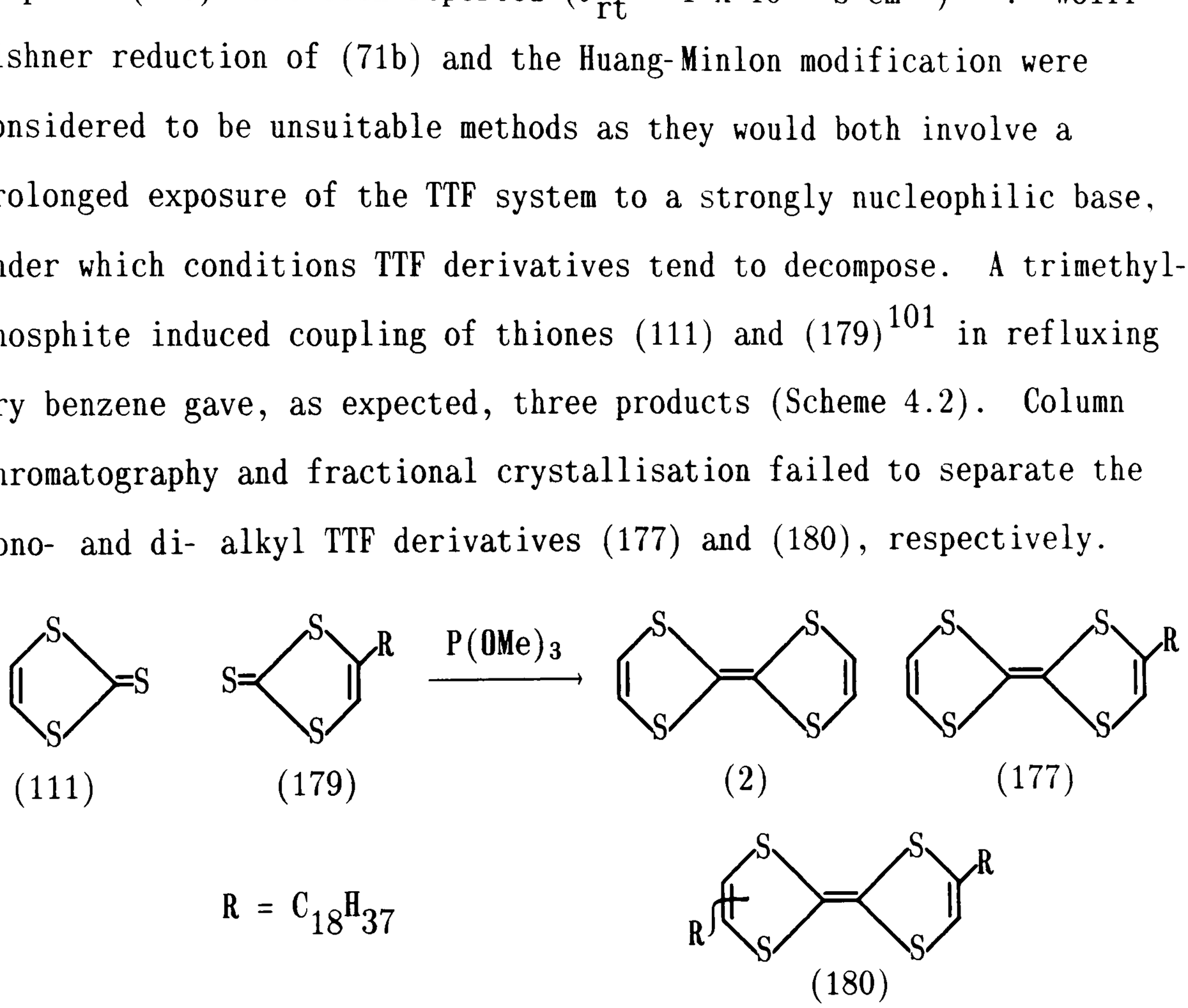


(176) $R=C_{17}H_{35}$ (177) $R=C_{18}H_{37}$ (178) $R=C_{17}H_{35}$

[1]High quality monolayer formation at the air-water interface requires high purity amphiphiles.

4.2.2 Attempted Synthesis of Monoalkyl-TTF (177)

Attempts to form monoalkyl-TTF derivative (177) by Clemmenson reduction of (71b) gave only moderate yields of the hydroxyl derivative (178), isolated as a yellow solid. No mass spectral or TLC evidence for the formation of compound (177) was found in the crude reaction mixture. Compound (178) had been previously prepared in our laboratory by lithium aluminium hydride reduction of (71b); LB films of the 1:1 TCNQ salt of compound (178) have been reported (σ_{rt} ~ 1 x 10^{-3} S cm^{-1})[156]. Wolff-Kishner reduction of (71b) and the Huang-Minlon modification were considered to be unsuitable methods as they would both involve a prolonged exposure of the TTF system to a strongly nucleophilic base, under which conditions TTF derivatives tend to decompose. A trimethyl-phosphite induced coupling of thiones (111) and (179)[101] in refluxing dry benzene gave, as expected, three products (Scheme 4.2). Column chromatography and fractional crystallisation failed to separate the mono- and di- alkyl TTF derivatives (177) and (180), respectively.



Scheme 4.2

A common method for the protection of ketones involves treatment with ethane-1,2-dithiol to give a cyclic dithioketal. The dithioketal may then be easily desulphurised with Raney-nickel giving the overall conversion C=O → CH_2. However, the carbonyl group of (71b) was

completely resistant to reaction with ethane-1,2-dithiol, or indeed ethane-1,2-diol, under a variety of conditions. This is a likely consequence of steric crowding in the reaction product. Thus, in summary, we have been unable to isolate a pure sample of monoalkyl-TTF (177).

4.2.3 Synthesis and Cyclic Voltammetry of TTF-Esters (181), (183)-(185) and (190)

We next turned our attentions to the synthesis of TTF linked to an alkyl chain through ester functionality; CV data for the known ethyl ester (181) ($E_1^{\frac{1}{2}}$ = 0.47, $E_2^{\frac{1}{2}}$ = 0.85 V)[154] indicated that we could expect these derivatives to have a similar donor ability to that of the alkanoyl-TTF derivatives (71) already studied in our laboratory.

4.2.3.1 Synthetic Strategies to TTF-Esters

As an initial strategy we investigated acid-catalysed esterification of TTF-carboxylic acid (182)[2] with alcohols. Thus, reactions of (182) for two hours in refluxing methanol, or ethanol, in the presence of concentrated sulphuric acid as dehydrating agent, proceeded smoothly to give the expected products, (183) and (181) respectively, as red solids (*ca.* 65% yield) (Scheme 4.3). Application of this methodology to longer chain alcohols, *viz.* 1-hexanol and 1-octanol, resulted in a dramatic reduction in the yields of the corresponding esters, (184) and (185) (*ca.* 5% yields), even after seven days at reflux. This unreactivity may derive from the sterically hindered conformations that can

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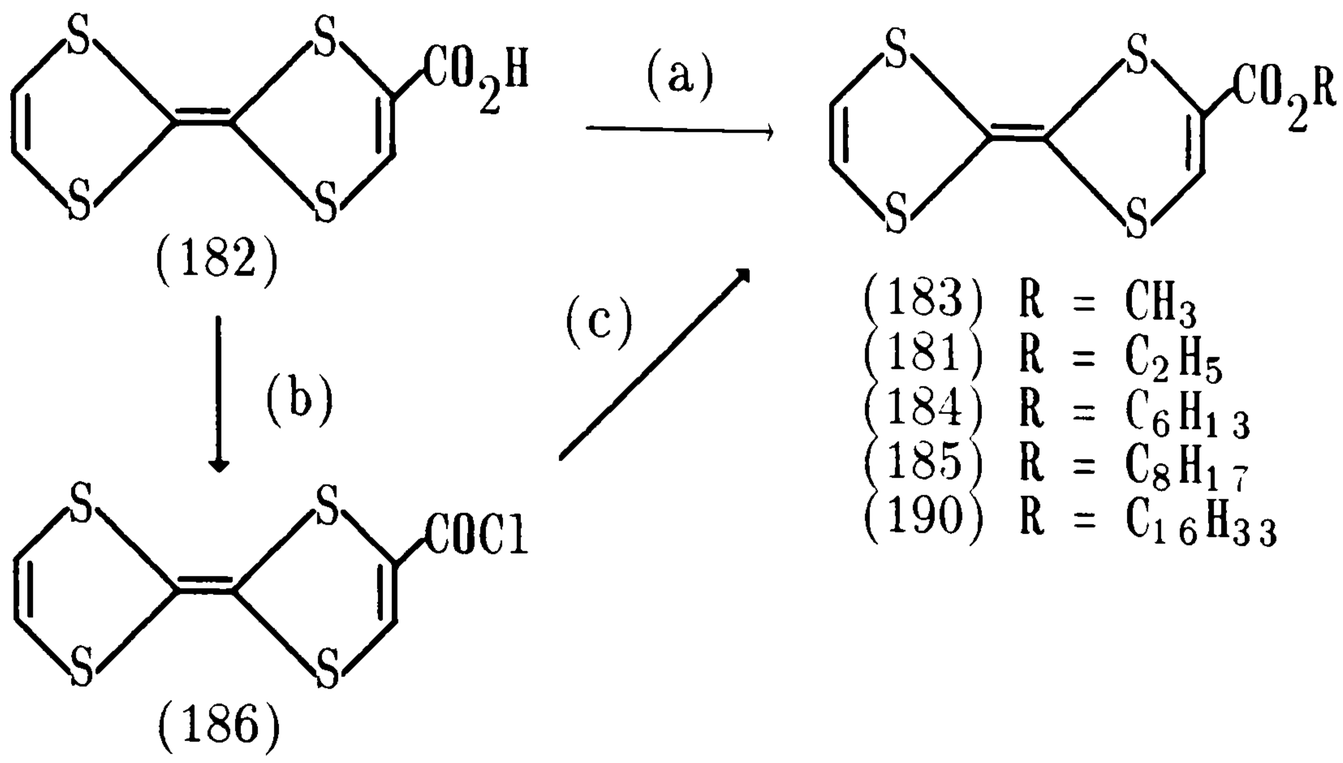
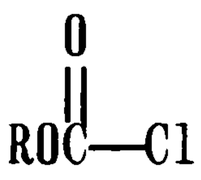
[2]Acid (182) was prepared by reaction of monolithio-TTF with solid carbon dioxide using the procedure described by Green (ref.154).

exist in the longer chain alcohols.

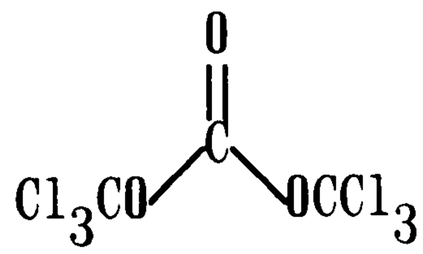


Scheme 4.3: *Reagents: (a) ROH/H_2SO_4; (b) $(COCl)_2$; (c) ROH, pyridine.*

To overcome this problem, the acid (182) was converted to the unstable acid chloride (186) by reaction with oxalyl chloride in benzene-acetonitrile (5:1 v/v) and a catalytic amount of DMF under conditions previously described by Panetta *et al.*[157]; reaction of equimolar amounts of (186), 1-hexanol and pyridine in dry dichloromethane gave, as anticipated, improved yields of ester (184) (*ca.* 15%). However, in order to further improve product yields, we resorted to direct reaction of monolithio-TTF (175) with alkylchloroformates. The longest chain chloroformate commercially available was the C_8 derivative (187), which on reaction with anion (175) gave ester (185) in 35% yield after purification. It was, thus, concluded that long chain alkylation of TTF through ester functionality was best achieved by reaction of monolithio-TTF (175) with alkylchloroformates, although purification is often difficult and time-consuming.



(187) R=C_8H_{17}
(189) R=$C_{16}H_{33}$



(188)

Chloroformates have, in the past, been prepared by reaction of an alcohol with an excess of phosgene[158]. However, due to its toxicity, phosgene is difficult to handle safely in the laboratory. Therefore, the phosgene substitute bis(trichloromethyl)carbonate (aka "triphosgene") (188) has been developed and has proved to be far safer and more convenient to handle[159]. Thus, slow addition of 1 equivalent of pyridine to a cooled solution of 1 equivalent of 1-hexadecanol and 1/3 equivalent of triphosgene in dry ether gave (189) as a colourless oil (86% yield). Treatment of monolithio-TTF (175) with an excess of chloroformate (189) at -78^{o}C, followed by warming to room temperature overnight, gave ester (190) (29% yield). Interestingly, ester (190) was found to crystallise in two forms, one of which is red (190a) ($\nu_{C=O}$ 1700 cm^{-1}) and the other yellow (190b) ($\nu_{C=O}$ 1720 cm^{-1}). The yellow form (190b) could be isolated by recrystallisation from a low boiling solvent (*eg.* methanol), the red form (190a) from a higher boiling solvent (*eg.* toluene). On warming the yellow form (190b) on a melting point slide a phase change is observed (45 - 50^{o}C) to give the thermodynamically less stable red form (190a) (mpt. 72^{o}C). The precise orientation of the alkyl chain around the ester group in the two isomers is unclear, but would seem to be the origin of this anomalous behaviour. It is notable that similar behaviour was not observed in the shorter chain homologues (184) and (185).

4.2.3.2 Cyclic Voltammetry of TTF-Esters

The electron donor ability of the esters (183), (184), (185) and (190) was investigated by cyclic voltammetry; the data are presented in Table 4.1, along with those for TTF. The voltammograms of ester (190) and TTF are compared in Figure 4.2.

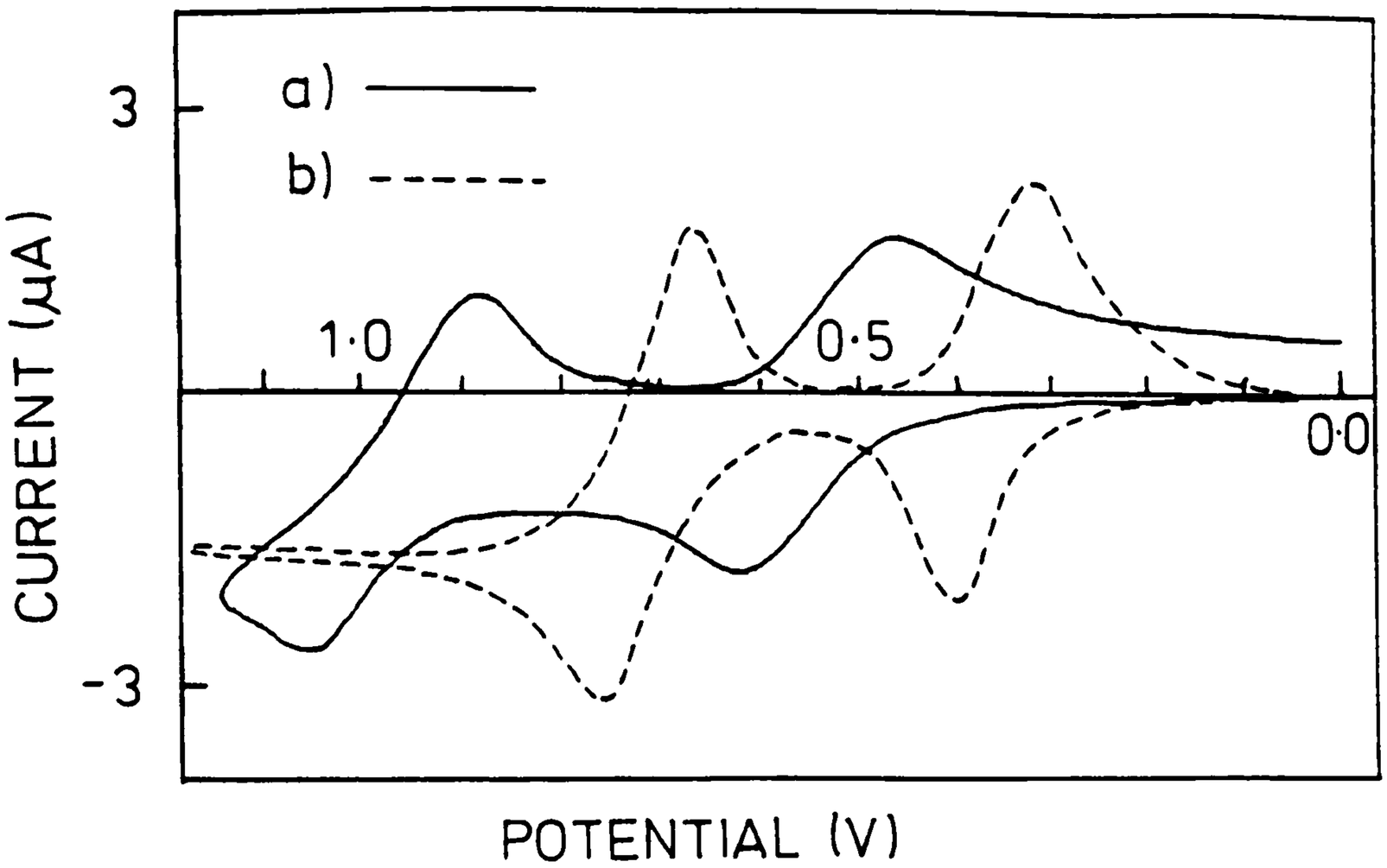


Figure 4.2: *Cyclic Voltammograms of (a) ester (190) and (b) TTF (2).*

COMPOUND	$E^{\frac{1}{2}}_1$	$E^{\frac{1}{2}}_2$
TTF	0.34	0.71
(183)	0.45	0.83
(181)	0.47	0.83
(184)	0.51	0.87
(185)	0.51	0.88
(190)	0.54	0.90

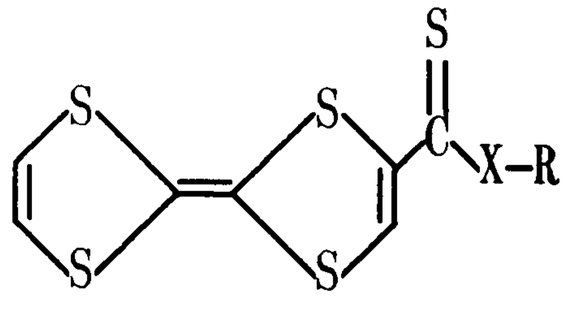
Table 4.1: *Cyclic voltammetry data for the TTF esters (181),(183)-(185) and (190); vs Ag/AgCl, Pt button electrode, scan rate = 100 mV sec^{-1}; 5 x 10^{-5} M donor, 0.1M $[Bu_4N][ClO_4]$ in MeCN.*

All the esters studied show two reversible, one-electron oxidation waves at a higher potential than those exhibited by TTF under identical conditions. This is indicative of reduced donor ability, relative to TTF, consistent with the attachment of the electron withdrawing ester group to the TTF skeleton. As predicted, the length of the alkyl chain has only a slight effect upon the oxidation potential of the esters, indicating that the electronic states of the homologous series of TTF

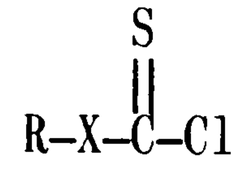
esters are not significantly affected by the size of the alkyl substituent. This follows precedents in other alkyl-substituted TTF derivatives[99].

4.2.4 Synthesis and Cyclic Voltammetry of TTF-Thioester (191)

Continuing with our initial aim of reducing the ionisation potential of the donor, we chose to investigate the thioester and dithioester TTF derivatives, (191) and (192) respectively, which should have lower ionisation potentials than ester (190).



(191) $R=C_{16}H_{33}$; X=O
(192) $R=C_{16}H_{33}$; X=S



(193) $R=C_{16}H_{33}$; X=O
(194) $R=C_{16}H_{33}$; X=S

Treatment of monolithio-TTF (175) with chlorothionoformate (193), prepared by reaction of an excess of thiophosgene with 1-hexadecanol and pyridine in dry ether, gave thioester (191) as a deep purple solid (38% yield). It is interesting that we have yet to observe any reaction between anion (175) and (194) [(194) was prepared analogously to (193) by reaction of thiophosgene with 1-hexadecylthiol], possibly indicating that the dithioester (192) is unstable. This conclusion was substantiated by the absence of isolable products on reaction of monolithio-TTF (175) with carbon disulphide after either acid or alkyl iodide work-up.

The cyclic voltammogram of thioester (192) (Figure 4.3) shows two reversible one-electron oxidation waves at a slightly lower potential than the corresponding ester (190) under identical conditions [*cf.* (192): $E_1^{\frac{1}{2}} = 0.49$, $E_2^{\frac{1}{2}} = 0.86$; (190): $E_1^{\frac{1}{2}} = 0.54$, $E_2^{\frac{1}{2}} = 0.90$ V] consistent with a reduction of electronegativity of the side-chain.

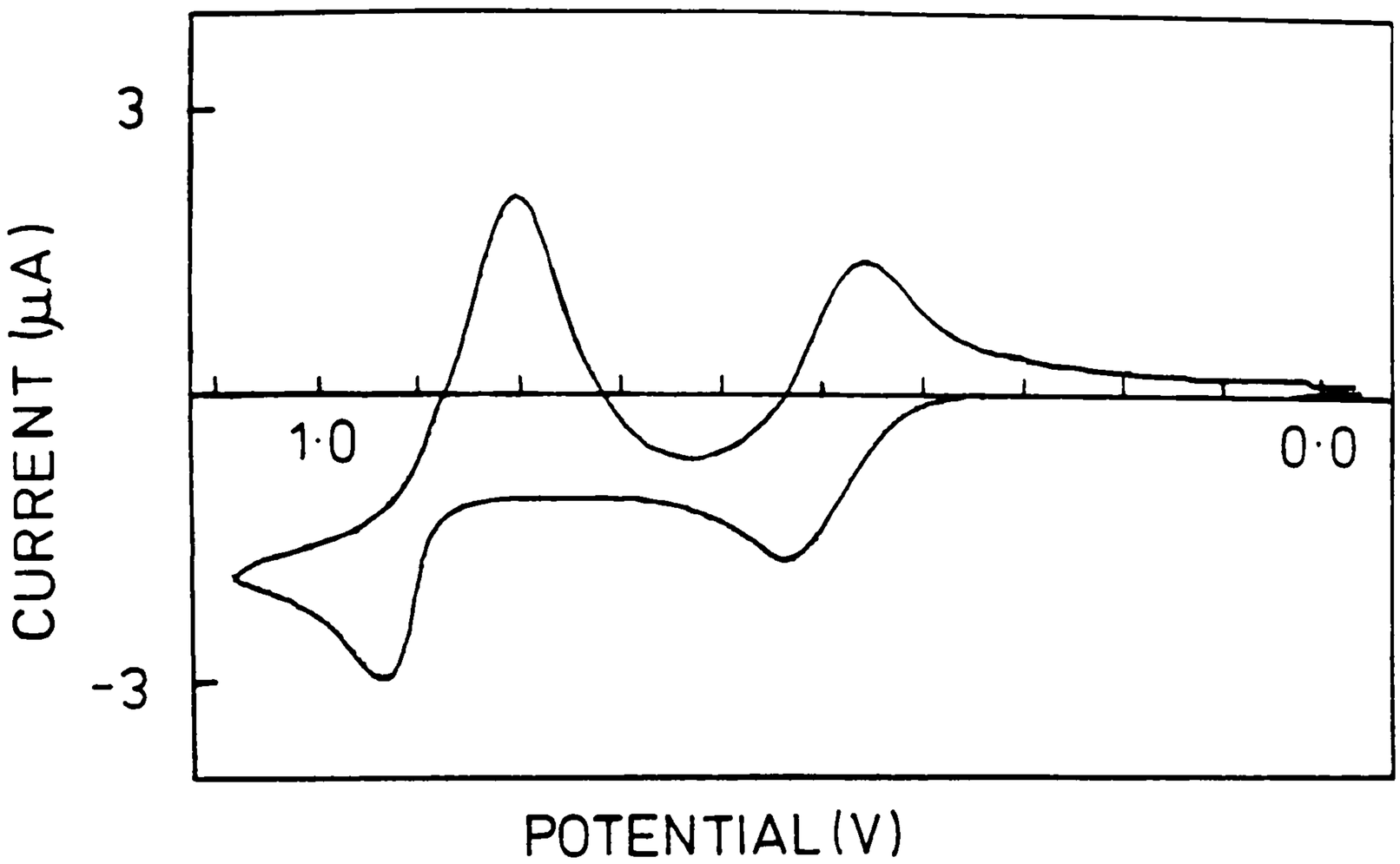


Figure 4.3: *Cyclic Voltammogram of thioester (191).*

4.3 LB FILM FORMATION

4.3.1 LB Films of TTF Ester (190a)

A fresh solution (100 μl of a *ca.* 2 x 10^{-3} M solution) of the red form of ester (190) in benzene was spread onto the surface of ultra-pure water. After evaporation of the solvent, the film was compressed using a mobile barrier at a rate of 5 cm^2 min^{-1}, while the surface pressure (π) versus molecular area (A) was monitored. The π vs A isotherm is shown in Figure 4.4. The monolayers of (190a) on the subphase surface were found to be very stable, as changes in the isotherm on repeated compression were minimal. The area per molecule in the condensed phase, assuming monolayer coverage of the subphase, was 0.23 ± 0.01 nm^2. This is in excellent agreement with the value for the cross-sectional area of the molecule, calculated from a conventional space-filling model (*ca.* 0.235 nm^2), indicating that the molecules are probably arranged with the alkyl chains nearly normal to the plane of the subphase.

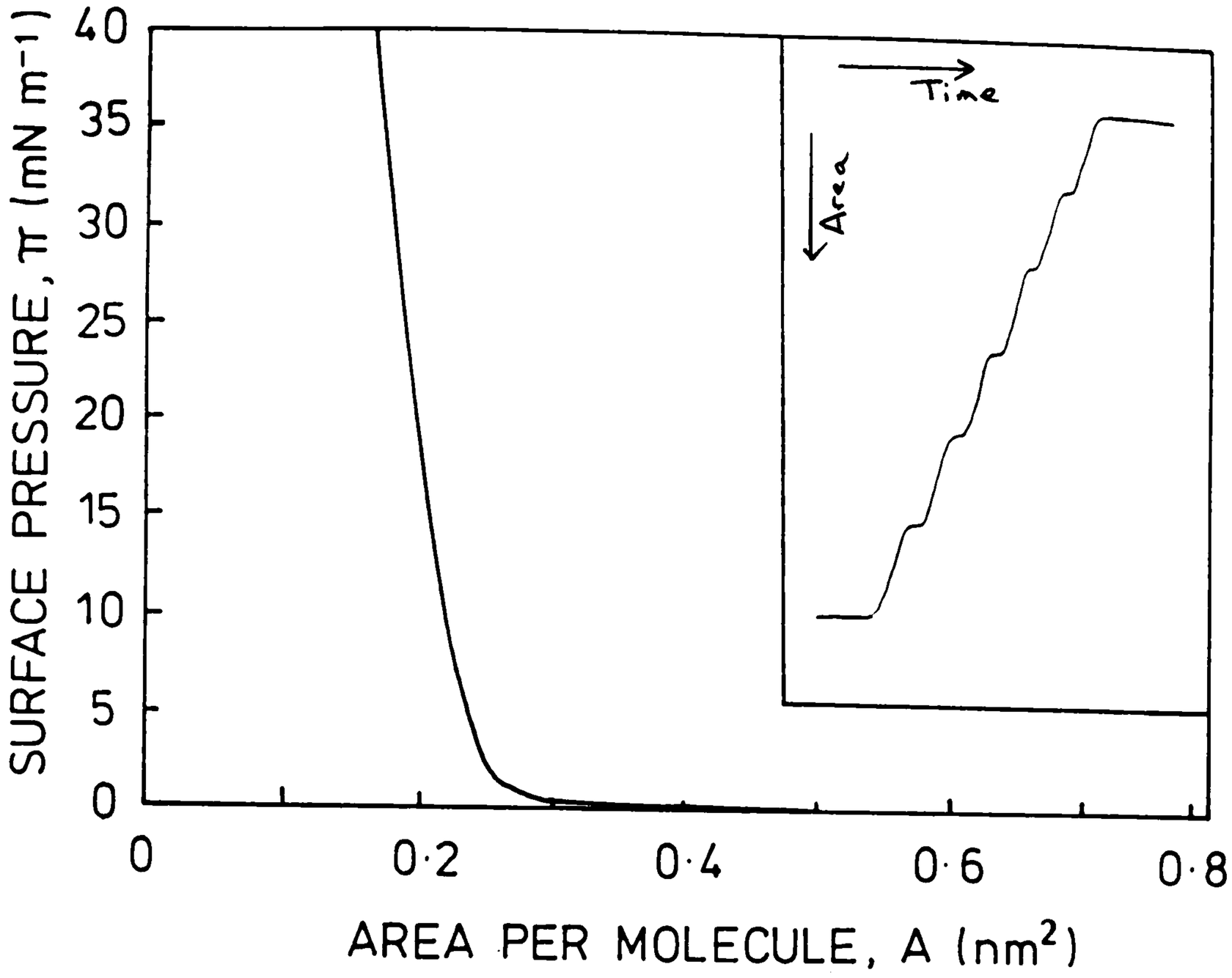


Figure 4.4: *Surface pressure vs molecular area isotherm for ester (190a); inset shows the dipping record of (190a) onto a glass substrate.*

"Y-Type" deposition of ester (190a) was achieved onto a clean glass substrate utilising a constant surface pressure of 30 mN m^{-1} and a dipping speed of approximately 1 cm min^{-1} on both inward and outward movements of the substrate. Films of greater than 30 monolayers have been assembled without any significant loss of quality and no detected collapse of the monolayer on the subphase. Visual inspection of the multilayers clearly showed excellent film uniformity with very few optically diffusing defects. The deposition ratio was ~ 0.75, showing that there is a greater monolayer pick-up on the outward movement of the substrate. A typical dipping record is shown in Figure 4.4 (inset).

The lateral d.c. room temperature conductivity of 25 layers of the as-deposited film was typically 1 x 10^{-4} S cm^{-1}, measured using a two-probe technique with air-drying silver paste contacts. Conductivities were measured with the contact gap varied between 4 and 10 mm,

the resistance measurements were found to be directly proportional to the separation, indicating that any resistance due to the silver paste contacts was negligible. No anisotropy of conductivity was observed in the plane of the substrate.

On exposure to iodine vapour for about 5 minutes in a sealed container, the orange film became brown-purple and a significant drop in conductivity to *ca.* 5×10^{-7} S cm^{-1} was noted; this is consistent with complete oxidation of the TTF-ester (190a). Following the exposure, the conductivity increased over a period of time, reaching a constant maximum value of 1×10^{-2} S cm^{-1} after 2 hours. The conductivity remained stable at this value for a number of days on standing in air. We rationalise this behaviour in terms of decomposition of the unstable fully oxidised TTF^{+} (I_3^{-}) system to a stable mixed-valence $TTF^{x+}(I_3^{-})_x$ system (where $x < 1$). Similar behaviour has been reported for films of hexadecanoyl-TTF (71a) studied in our laboratory[105]. Highly conducting mixed-valence halide systems are well-documented for crystalline TTF systems *eg.* $TTFBr_{0.71}$ $\sigma_{rt} \sim 800$ S cm^{-1} [19].

4.3.2 Preliminary Investigations of monolayers of TTF Esters (184), (185) and (190b)

The π vs A isotherm for the yellow form of (190) (100 μl of *ca.* 2×10^{-3} M solution in chloroform) is shown in Figure 4.5. The first compression shows a reproducible plateau observed at a surface pressure of *ca.* 20 mN m^{-1}. On the second compression an isotherm indicating stable monolayer formation is obtained (area per molecule 0.22 ± 0.01 nm^2). Subsequent compression reproduces this isotherm without significant modification. We have rationalised this behaviour in terms of an initial alignment with the long axis of the TTF skeleton parallel

to the water surface. It is possible that this alignment may be concomitant with a phase change of the ester (190), yellow to red: however, direct confirmation of this requires detailed infrared spectroscopic investigation of the films assembled at low surface pressures [<20 mN m^{-1}] and high surface pressures [>25 mN m^{-1}], with specific reference to carbonyl stretching frequencies: these are known to be different for the red and yellow crystalline forms of (190). LB films of the yellow form of (190) have not yet been investigated.

Stable monolayers of esters (184) and (185) could not be obtained on the surface of the subphase, almost certainly due to the shorter chain lengths of the alkyl chains.

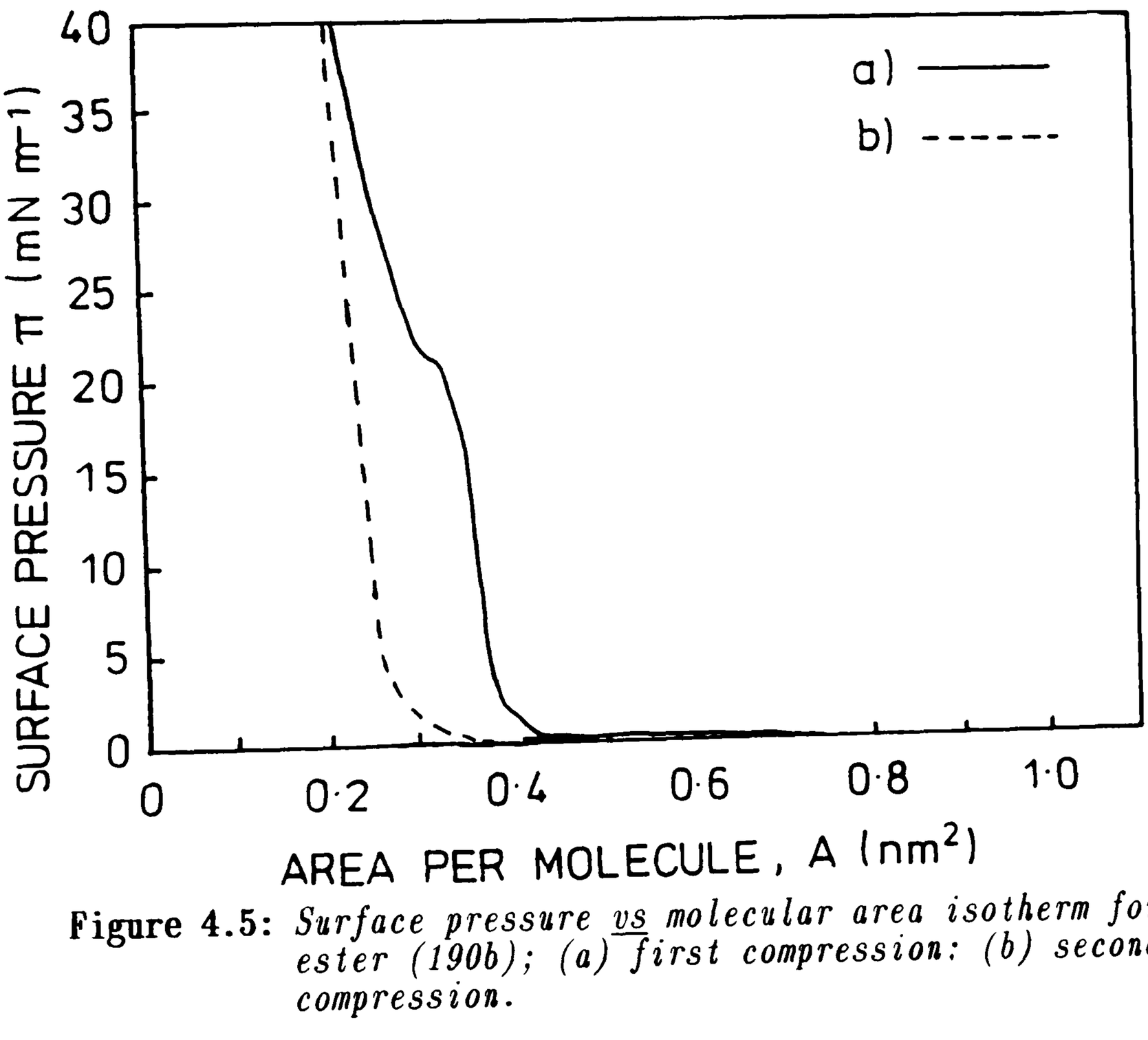


Figure 4.5: *Surface pressure vs molecular area isotherm for ester (190b); (a) first compression: (b) second compression.*

4.3.3 LB Films of TTF-Thioester (191)

A solution of thioester (191) in chloroform (*ca.* 2 x 10^{-3} M) was used for spreading the material onto the surface of ultra-pure water. The π vs A isotherm is shown in Figure 4.6; the area per molecule in the condensed phase was 0.18 ± 0.01 nm^2. Changes in the isotherm on repeated compression were minimal. The low area per molecule (*cf.* 0.235 nm^2 calculated empirically) may be indicative that either the layer on the water surface is more than one molecule thick in places, or that the thioester (191) is slightly impure.

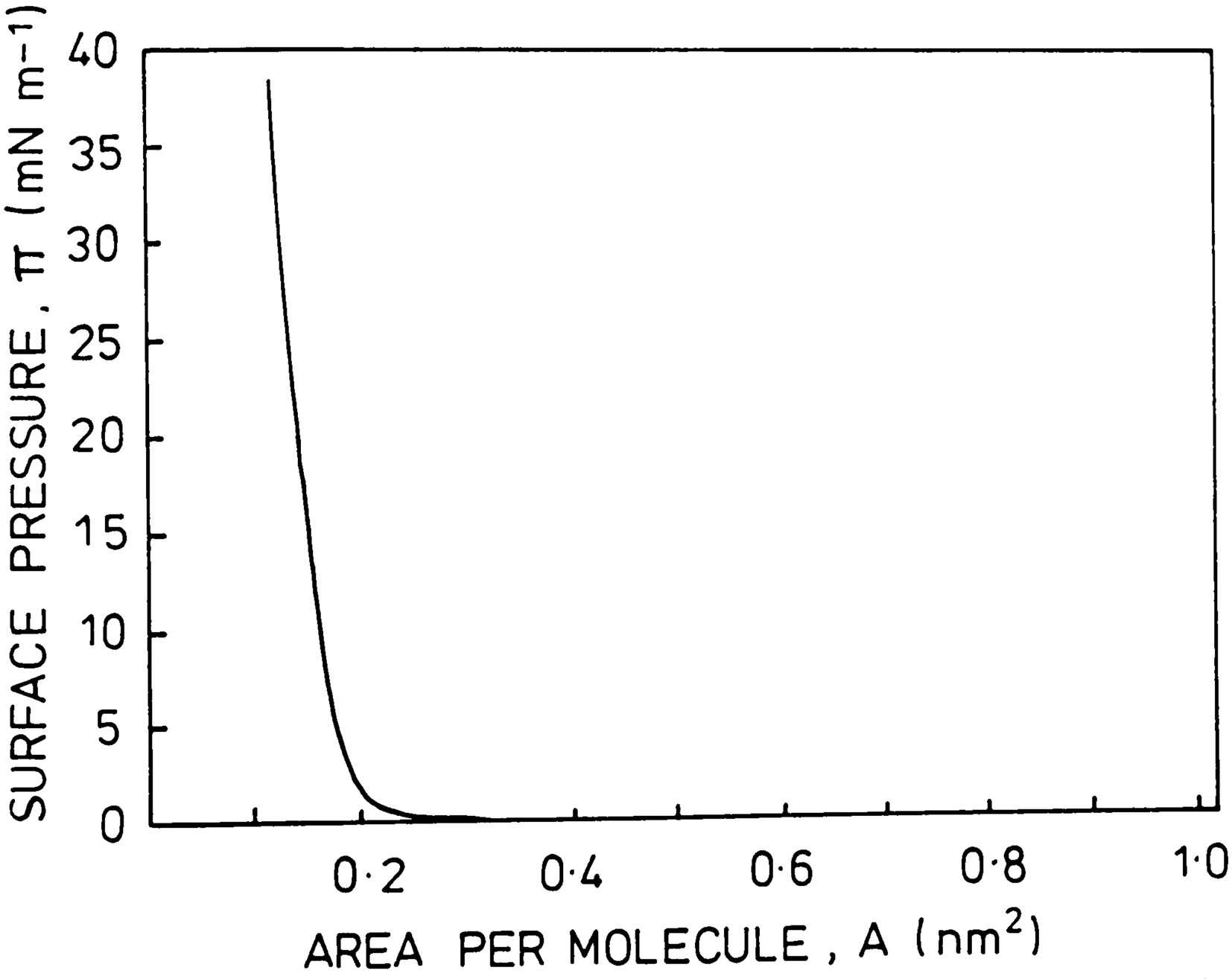


Figure 4.6: *Surface pressure vs molecular area isotherm for thioester (191).*

Nevertheless, if the surface pressure was carefully controlled at 30 mN m^{-1}, multilayers of (191) could be assembled on a clean glass substrate ("Y-type" deposition, deposition ratio 0.8), typically using dipping speeds of 1 cm^2 min^{-1}. The lateral d.c. conductivity of the as-deposited film was notably high, typically σ_{rt} = 5 x 10^{-2} S cm^{-1} for 25

multilayers. On exposure to iodine vapour there was a slight decrease in conductivity to 1 x 10^{-3} S cm^{-1}, whereupon the conductivity rose to as high as 0.6 S cm^{-1} after about two hours. This behaviour is again consistent with the formation of a mixed-valence $TTF^{x+}(I_3^-)_x$ ($x < 1$) film. This conductivity value represents the highest documented conductivity to date for a doped LB film of a TTF derivative.

Preliminary variable temperature conductivity measurements in the range 300-77 K for the iodine-doped film of thioester (191) have shown it to be semiconducting with an activation energy of 0.095 eV. Such a low activation energy eliminates an ionic conduction mechanism *via* iodine; indeed I_3^- ions present in the fully oxidised films give rise to poor conductivity. Thus, I_3^- physically held in the LB film matrix plays little, if any, part in the conductivity process. We conclude, therefore, that the conduction is an electronic process *via* the TTF moiety.

4.4 CONCLUSIONS

Synthetic routes to amphiphilic monofunctionalised TTF derivatives with alkyl groups attached directly to the TTF ring, or through ester, thioester and thioketone functionality have been investigated. Ester (190) and thioester (191) form stable monolayers on the surface of ultra-pure water, and high quality LB films (Y-type) have been assembled on hydrophobic glass substrates. In both cases, the conductivity of the multilayers falls upon iodine doping, but increases with time following exposure - the conductivity of the doped films of thioester (191) (σ_{rt} ~ 0.6 S cm^{-1}) is the highest reported for an LB film of a TTF derivative.

CHAPTER FIVE

TCNQ SALTS OF CYCLIC SULPHONIUM CATIONS

5.1 INTRODUCTION

The first organic salts based on the anion-radical of TCNQ were prepared in the early 1960's by workers at Du Pont research laboratories. A number of these early salts, such as quinolinium-$(TCNQ)_2$, exhibited unprecedented electrical conductivities for organic materials (σ_{rt} = 1 x 10^{-2} - 10 S cm^{-1}); the majority, however, showed typical insulating or semiconducting characteristics. Literally thousands of TCNQ salts have since been prepared, whose novel electronic and magnetic properties have been the subject of intense interest. Close face-to-face overlap of the TCNQ molecules within the crystal lattice favours extensive intermolecular electron mobility and the formation of an energy band. The partial occupancy of this energy band is a pre-requisite for high conductivity; this usually arises as a result of partial charge-transfer from donor to acceptor (*eg.* TTF-TCNQ, ρ = 0.59), or by crystallisation of a binary salt in a stoichiometry other than 1:1, for example $(cation)^+(TCNQ)_2^-$. Varying the cation in TCNQ salts affects the stoichiometry, the degree of charge-transfer and the stacking mode of the crystal, providing an enormous range of electronic behaviour. Classical examples of organic metals and semiconductors are provided by the widely studied ammonium and phosphonium cation salts of TCNQ. These cations form C-T salts with TCNQ by virtue of the iodide counterion serving as the electron source for the formation of $(TCNQ)_n^{\bullet -}$. The iodide is oxidised to free iodine, which, in practice, is often scavenged as the triiodide ion, I_3^- (Equation 5.1). Indeed, a number of ammonium-TCNQ salts have been found to have ternary composition as a result of iodine incorporation, *viz.* $(R_3NH)^+(TCNQ)^{-2/3}(I_3^-)_{1/3}$[160,161].

$$3M^+I^- + 2n\ TCNQ \longrightarrow 2M^+(TCNQ)_n^- + MI_3^- \qquad (5.1)$$

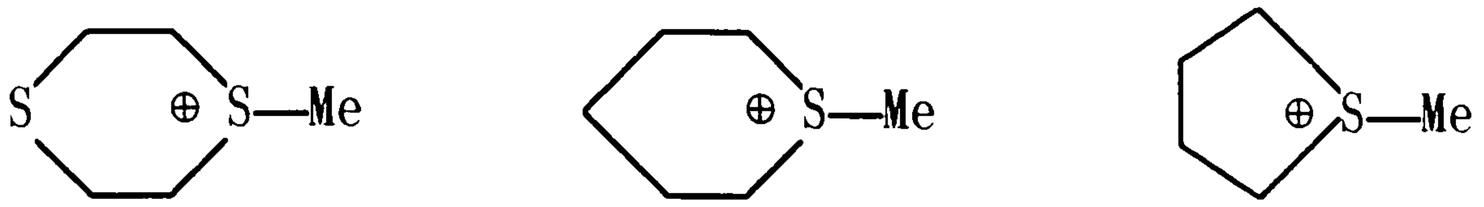
5.2 TCNQ SALTS OF SULPHUR-BASED CATIONS

Although there is a considerable literature devoted to ammonium and phosphonium cation salts of TCNQ, there has been remarkably little interest in TCNQ salts of sulphonium cations. A 1:2 binary salt (195) of the triphenylsulphonium cation with TCNQ (σ_{rt} = 1 S cm^{-1}) was reported in early patent literature[162], and more recently, data on trialkylsulphonium cation salts of TCNQ (196)-(199) has emerged (Table 5.1)[163,164]. This latter class of salts exhibit both binary 1:2 and ternary composition, depending on the nature of the alkyl groups. An analogous ternary trimethylselenolium cation salt of TCNQ (200) has also been investigated[164]. The ternary salts show room temperature conductivities which are several orders of magnitude greater than the binary salts (Table 5.1), corresponding to a favourable modification of the conduction band. Preliminary X-ray analysis of the ternary sulphonium-TCNQ salts (198) and (199), has shown them to be isostructural with the most thoroughly studied ternary salt, the trimethylammonium cation salt of TCNQ (201)[160,161,165].

	COMPOUND	σ_{rt} (S cm^{-1})
(195)	$(Ph_3S)^+(TCNQ)_2^-$	1
(196)	$(Et_3S)^+(TCNQ)_2^-$	1.5 x 10^{-4}
(197)	$(Et_2MeS)^+(TCNQ)_2^-$	4 x 10^{-3}
(198)	$(EtMe_2S)^+(TCNQ)^{-2/3}(I_3^-)_{1/3}$	90
(199)	$(Me_3S)^+(TCNQ)^{-2/3}(I_3^-)_{1/3}$	40
(200)	$(Me_3Se)^+(TCNQ)^{-2/3}(I_3^-)_{1/3}$	25
(201)	$(Me_3NH)^+(TCNQ)^{-2/3}(I_3^-)_{1/3}$	20

Table 5.1: *Stoichiometries and conductivities of known sulphonium cation salts of TCNQ.*

The potential of saturated sulphur heterocycles as cations for TCNQ salts has been virtually ignored, although unsaturated sulphur heterocycles are widely used as π-donors for TCNQ salts (*eg.* TTF-TCNQ, TMTTF-TCNQ). We, therefore, investigated cyclic sulphonium cations (202)-(204), which we find yield the binary (cation)$^{+}$(TCNQ)$_2^{-}$ salts (205)-(207)[166].



(202) $I^{\ominus}$ (205) $(TCNQ)_2^{\bullet-}$ (203) $I^{\ominus}$ (206) $(TCNQ)_2^{\bullet-}$ (204) $I^{\ominus}$ (207) $(TCNQ)_2^{\bullet-}$

5.3 PREPARATION OF CYCLIC SULPHONIUM CATION SALTS OF TCNQ (205)-(207)

The cyclic sulphonium iodides (202)[167], (203)[168] and (204)[168] were all prepared according to literature methods by simple alkylation of the appropriate sulphide with methyl iodide in methanol (quantitative yields). Black-blue crystals of the (cation)$^{+}$(TCNQ)$_2^{-}$ salts (205)-(207) were prepared in moderate yield (40 - 60%) by mixing the appropriate sulphonium methiodide with TCNQ in hot, dry acetonitrile, followed by slow cooling to 0^{o}C. The stoichiometry of the salts (205)-(207) was determined by elemental analysis and found to be consistent with a 1:2 binary composition. Lequan *et al.* have correlated the formation of binary 1:2 and ternary 1:1:(triiodide)$_{1/3}$ TCNQ salts of sulphonium cations with the degree of crowding experienced by the sulphur atom: the greater the crowding by substituents, the more likely a 1:2 salt will be isolated[163]. A similar correlation has also been proposed for the ammonium cation salts of TCNQ. Whilst this hypothesis appears to hold for salts (205)-(207), having similar degrees of crowding of the sulphur atom as the cation in the 1:2 salt $Et_2MeS(TCNQ)_2$ (197) studied by Lequan

et al.[163], it must be stressed that the observed stoichiometry is driven solely by crystal packing effects. Indeed, the reasons for I_3^- incorporation into the lattice of some salts are still unclear.

Conductivity of salts (205)-(207)

Variable temperature conductivity measurements in the range 300-77K show that all three salts (205)-(207) are semiconducting, *ie.* there is a steady decrease in conductivity as the temperature is lowered. The room temperature conductivities (σ_{rt}) for salts (205)-(207) (Table 5.2) are notably higher than those for most binary TCNQ salts of ammonium and phosphonium cations (typically, σ_{rt} = 1 x 10^{-5} - 1 x 10^{-2} S cm^{-1}), and are also significantly higher than those of the known binary TCNQ salts of sulphonium cations (195)-(199) (Table 5.1)[163,164]. The σ_{rt} value for salt (207) was obtained as a compressed pellet; these measurements tend to be lower than for single crystals, since the former are subject to the effects of electrical resistance associated with imperfect interparticle contact[134].

SALT	Cation:TCNQ	σ_{rt} (S cm^{-1})
(205)	1:2	2.0[a]
(206)	1:2	0.1[a]
(207)	1:2	0.001[b]

Table 5.2: *Conductivities of cyclic sulphonium cation salts (205)-(206) of TCNQ; (a) single crystal, four-probe measurement; (b) compressed pellet, two-probe measurement.*

5.4 X-RAY STRUCTURE OF MDT(TCNQ)$_2$, (205)

The single crystal X-ray structure of MDT(TCNQ)$_2$ (205), the most highly conducting member of the series of salts (205)-(207), has been successfully refined[1]. The TCNQ molecules form discrete dimer pairs (Figure 5.1a); the intra-dimer [TCNQ(1)-TCNQ(2)] separation between the mean planes of the TCNQ molecules is 3.2Å, and the intra-dimer configuration is of the "ring-over-bond" type (Figure 5.1b).

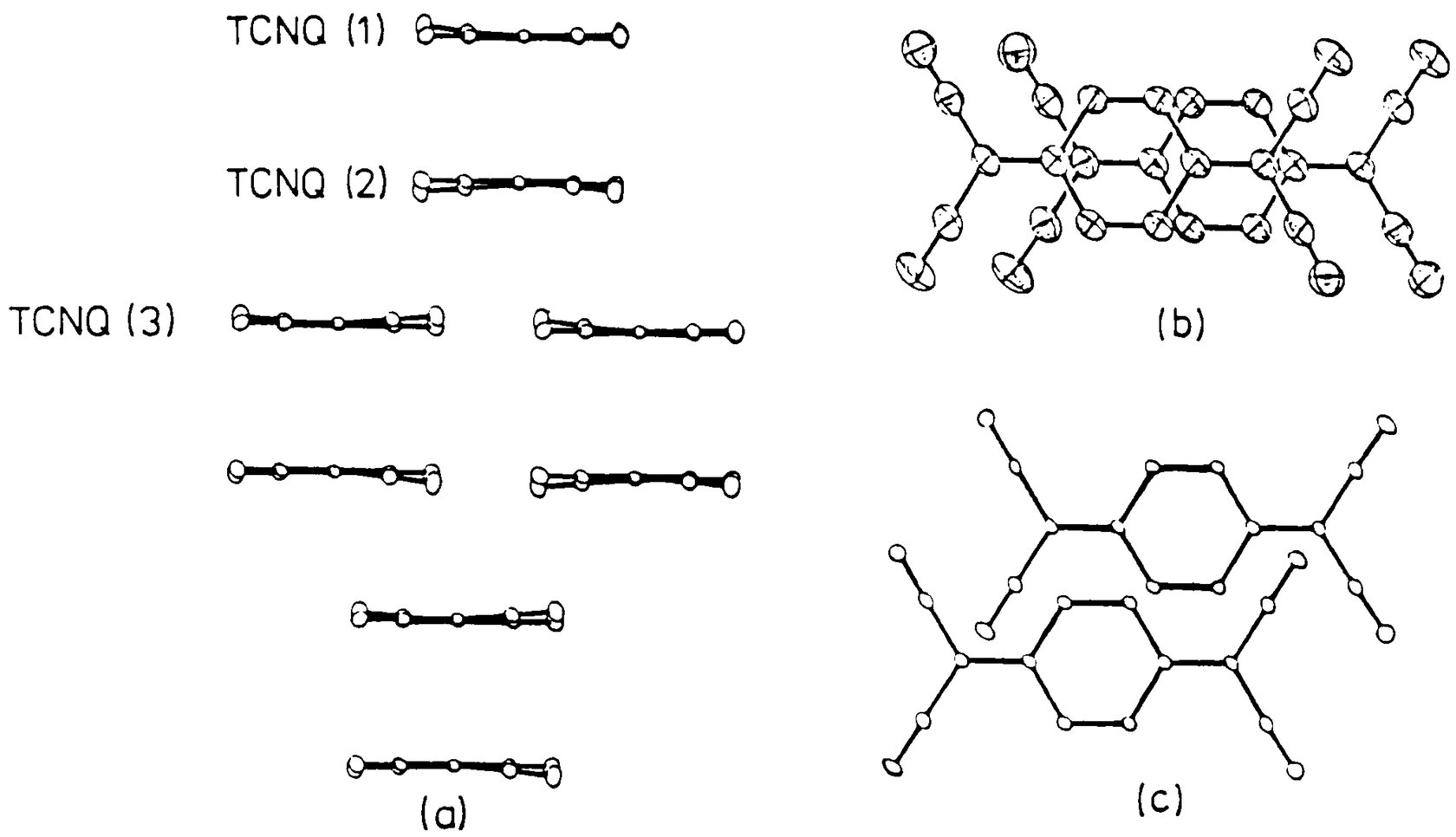


Figure 5.1: *X-Ray structure of MDT(TCNQ)$_2$ (205); (a) TCNQ dimers viewed down the long axis of the TCNQ molecules, showing "brick wall" stacking arrangement; (b) Intradimer TCNQ(1)-TCNQ(2) overlap and (c) interdimer TCNQ(2)-TCNQ(3) overlap, as seen perpendicular to the TCNQ plane.*

This intra-dimer configuration is common and is known[169] to maximise the attractive interactions within a pair of TCNQ ions, $(TCNQ)_2^{\bullet-}$. However, there is essentially no inter-dimer face-to-face overlap (Figure 5.1c), the strongly slipped inter-dimer configuration allows only weak interaction between neighbouring TCNQ molecules belonging to different dimers, *eg.* TCNQ(2) and TCNQ(3) (Figure 5.1a). This most unusual arrangement leads to a "brick-wall" stacking of TCNQ dimers within the

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[1]Crystallographic studies on MDT(TCNQ)$_2$ were performed by P. Bates and Prof. M.B. Hursthouse, Queen Mary College, London.

lattice when viewed perpendicular to the anion plane, as opposed to the more usual columnar stacking that is a feature of the vast majority of TCNQ salts.

The cavities formed by the TCNQ network are occupied by the MDT cations (Figure 5.2), the ring of which is, predictably, in the stable chair conformation. Non-bonded S··N distances are slightly asymmetric. however, all such distances are greater than the sum of the respective Van der Waal's radii, *viz.* 3.35Å[136]. This is a clear indication of little, if any, MDT··TCNQ interaction.

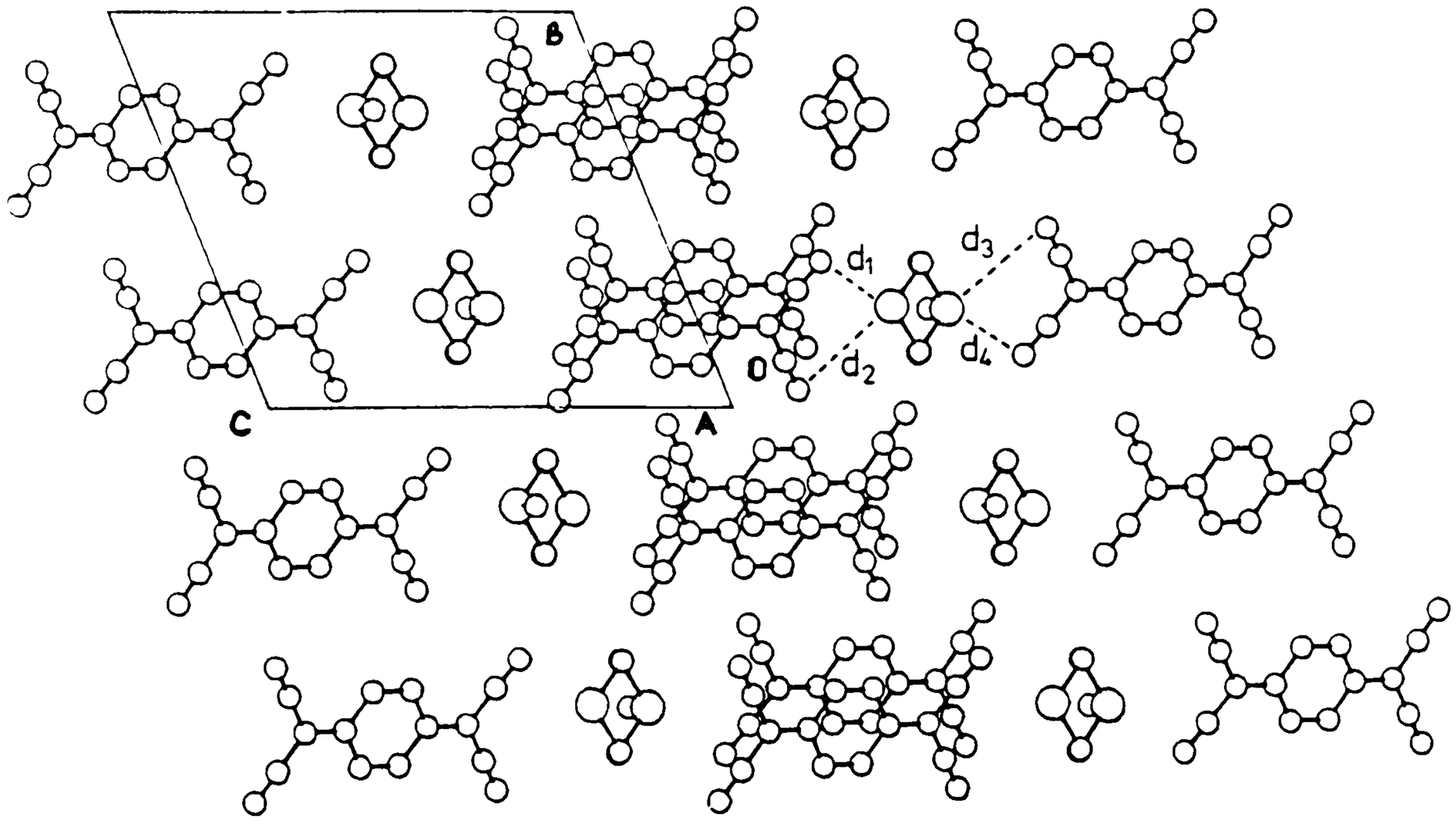
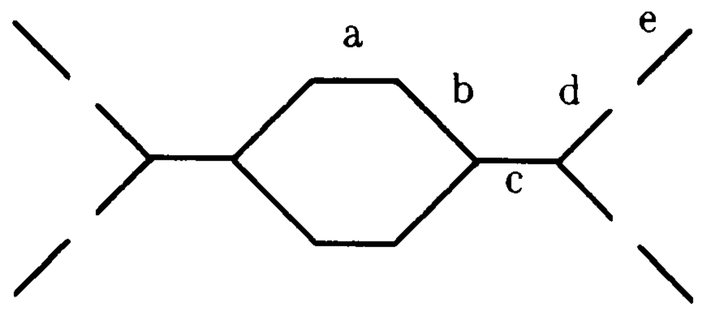


Figure 5.2: *X-Ray structure of MDT(TCNQ)$_2$ (205); View along the crystallographic a-o axis. Non-bonded S··N distances: d_1 = 3.74, d_2 = 3.98, d_3 = 4.14 and d_4 = 3.97 Å.*

The overall features of the structure are reminiscent of the -160^{o}C structure of the 1:2 salt N-methyl-N-ethylmorpholinium $(TCNQ)_2$, MEM-$(TCNQ)_2$, where weak, slipped inter-dimer interaction is also found[170]. However, above room temperature, MEM$(TCNQ)_2$ has a quite different structure[171]. The MEM$(TCNQ)_2$ salt has been thoroughly studied because of the unusual paramagnetic properties (a spin-Peierls transition) observed at low temperature[172].

Analysis of the bond lengths of the TCNQ moiety in TCNQ salts is a commonly employed technique for determining the degree of charge-transfer (ρ), as neutral TCNQ has significantly different bond lengths from that of anionic $TCNQ^{173}$. The bond lengths of the two independent TCNQ moieties within a dimer pair, *viz.* TCNQ(1) and TCNQ(2), in MDT-$(TCNQ)_2$ (205) are compared with those for $TCNQ^0$, $TCNQ^{\frac{1}{2}-}$ and $TCNQ^{\bullet-}$ in Table 5.3[174].



	BOND (Å)				
	a	b	c	d	e
$TCNQ^0$ a	1.346(4)	1.448(3)	1.374(4)	1.440(3)	1.138(3)
$TCNQ^{\frac{1}{2}-}$ a	1.355(4)	1.433(8)	1.396(9)	1.424(4)	1.145(5)
$TCNQ^{\bullet-}$ a	1.362(11)	1.424(9)	1.413(10)	1.417(6)	1.199(7)
TCNQ(1)	1.356(6)	1.430(6)	1.398(6)	1.420(6)	1.144(6)
TCNQ(2)	1.357(6)	1.434(6)	1.389(6)	1.421(6)	1.147(6)

Table 5.3: *Variation in TCNQ bond lengths with degree of charge transfer; (a) Data taken from reference 174.*

The data are wholly consistent with each TCNQ in a dimer pair being present as $TCNQ^{\frac{1}{2}-}$, there being no significant differences in bond lengths between TCNQ(1) and TCNQ(2) at this level of refinement (R = 0.060). However, from a view of strong electron correlation effects between electrons on the same and nearest neighbour molecules, it seems more reasonable that both $TCNQ^0$ and $TCNQ^{\bullet-}$ coexist in a dimer pair, with a rapid fluctuation of electrons between the TCNQ's. This, on the X-ray scattering experiment timescale, would give rise to the apparent equivalence of TCNQ's within each dimer. From the X-ray data it can,

however, be deduced that ρ = 1/2, and we can expect the conduction band formed along each stack to be half-filled.

5.5 OPTICAL ABSORPTION SPECTRA OF SALTS (205)-(207)

Electronic absorption measurements on TCNQ salts are a sensitive probe of the electronic interactions taking place in the solid-state. The FT-IR and UV-visible spectra of salts (205)-(207) were obtained, and have been analysed based on the results of studies on other TCNQ salts[18,118].

(i) Infrared Spectra

The infrared spectra of salts (205)-(207) are all very similar, showing the characteristic broad absorptions typical of a conducting C-T salt. In particular, the nitrile stretching frequencies of salts (205)-(207) are worthy of note - there are three moderate-strong absorptions for each salt (Table 5.4) indicating three different types of environment for the nitrile groups in salts (205)-(207).

SALT	$\nu_{C\equiv N}$ (cm^{-1}) [a]		
(205)	2167	2179	2198
(206)	2160	2180	2199
(207)	2166	2179	2196

Table 5.4: *Stretching frequencies of nitrile absorptions in the FT-IR spectra of salts (205)-(207); (a) Solids embedded in a KBr disc.*

The stretching frequencies of the nitrile group in TCNQ salts are reported to be linearly correlated with the degree of charge-transfer (ρ), and to occur between that of neutral TCNQ ($\nu_{C\equiv N}$ = 2227 cm^{-1}) and

fully ionic TCNQ ($\nu_{C\equiv N}$ = 2185 cm^{-1})[18]. The absorptions of salts (205)-(207) do not conform well to this correlation, each having two stretching frequencies below 2185 cm^{-1}, precluding any useful analysis in terms of ρ. This effect may be due to poor screening, in the absence of highly mobile conducting electrons.

(ii) UV-Visible Spectra

The solid-state UV-visible data for salts (205)-(207) are again strikingly similar (Table 5.5), showing four absorptions characteristic of mixed-valence TCNQ salts, commonly denoted A,B,C and D[118].

SALT	ABSORPTION (nm) [a]			
	A	B	C	D
(205)	2340	1040 920	665	400
(206)	2330	1025 880	645	395
(207)	2290	1025 900	670	400

Table 5.5: *Absorptions of the characteristic peaks, A-D, in the solid state UV-visible spectra of salts (205)-(207); (a) Nujol mull of solids, CaF_2 plates.*

The peaks B, C and D are assigned to intramolecular processes, specifically intramolecular transitions in $TCNQ^{\bullet -}$ (peaks B and D) and $TCNQ^{0}$ (peak C). Peak A is commonly observed in TCNQ salts which have $TCNQ^{0}$ in the conducting chain. This peak is associated with charge fluctuations along the TCNQ stacks:

$$TCNQ^{\bullet -} + TCNQ^{0} \longrightarrow TCNQ^{0} + TCNQ^{\bullet -}$$

In metallic TCNQ salts, peak A is observed at longer wavelength (*ie.* lower energy), typically around 2750 nm, indicating a more energetically favourable pathway for charge movement along the chain than is found in salts (205)-(207).

Although simplistic, our analysis of UV-visible spectra serves to show the presence of $TCNQ^{0}$ and $TCNQ^{\bullet-}$ in the TCNQ stacks of salts (205)-(207). This is clearly opposed to the equivalent $TCNQ^{\frac{1}{2}-}$ in each dimer pair indicated by X-ray analysis of $MDT(TCNQ)_2$ (205).

5.6 MAGNETIC PROPERTIES OF SALTS (205)-(207)

The three sulphonium salts (205)-(207) are strongly paramagnetic. The room temperature magnetic susceptibilities are given in Table 5.6.

SALT	$\chi^{\text{total b}}_{300K}$	$\chi^{\text{diamag a,b}}_{300K}$	$\chi^{\text{paramag b}}_{300K}$
(205)	+ 6.5 x 10^{-4}	- 2.9 x 10^{-4}	+ 9.4 x 10^{-4}
(206)	+ 6.1 x 10^{-4}	- 2.9 x 10^{-4}	+ 9.0 x 10^{-4}
(207)	- 0.2 x 10^{-4}	- 2.8 x 10^{-4}	+ 2.6 x 10^{-4}

Table 5.6: *Room temperature magnetic susceptibility data for salts (205)-(207); (a) Calculated from Pascals constants; (b) Units, emu* mol^{-1}.

The temperature dependence of the spin susceptibility has been extensively investigated by co-workers[2] using ESR (300 - 90K) and a Faraday balance (380-4.7K)[175]. The data for salts (206) and (207) are consistent with Curie-Weiss behaviour, typical of many cation-TCNQ salts. The weak paramagnetism of salt (207) suggests that the $TCNQ^{\bullet-}$ spins couple antiferromagnetically. On the other hand, data for $MDT(TCNQ)_2$ (205) are strikingly different[176]: the susceptibility is found to increase with decreasing temperature before passing through a broad maximum at *ca.* 100K. At 5.5K there is a sharp fall in the susceptibility with a 25% fall in magnitude between 5.5K and 4.7K, the lower limit of the experiment.

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[2]Magnetic susceptibility measurements were performed by Dr. S.D. Obertelli and Dr. R.H. Friend, Cavendish Laboratories, Cambridge.

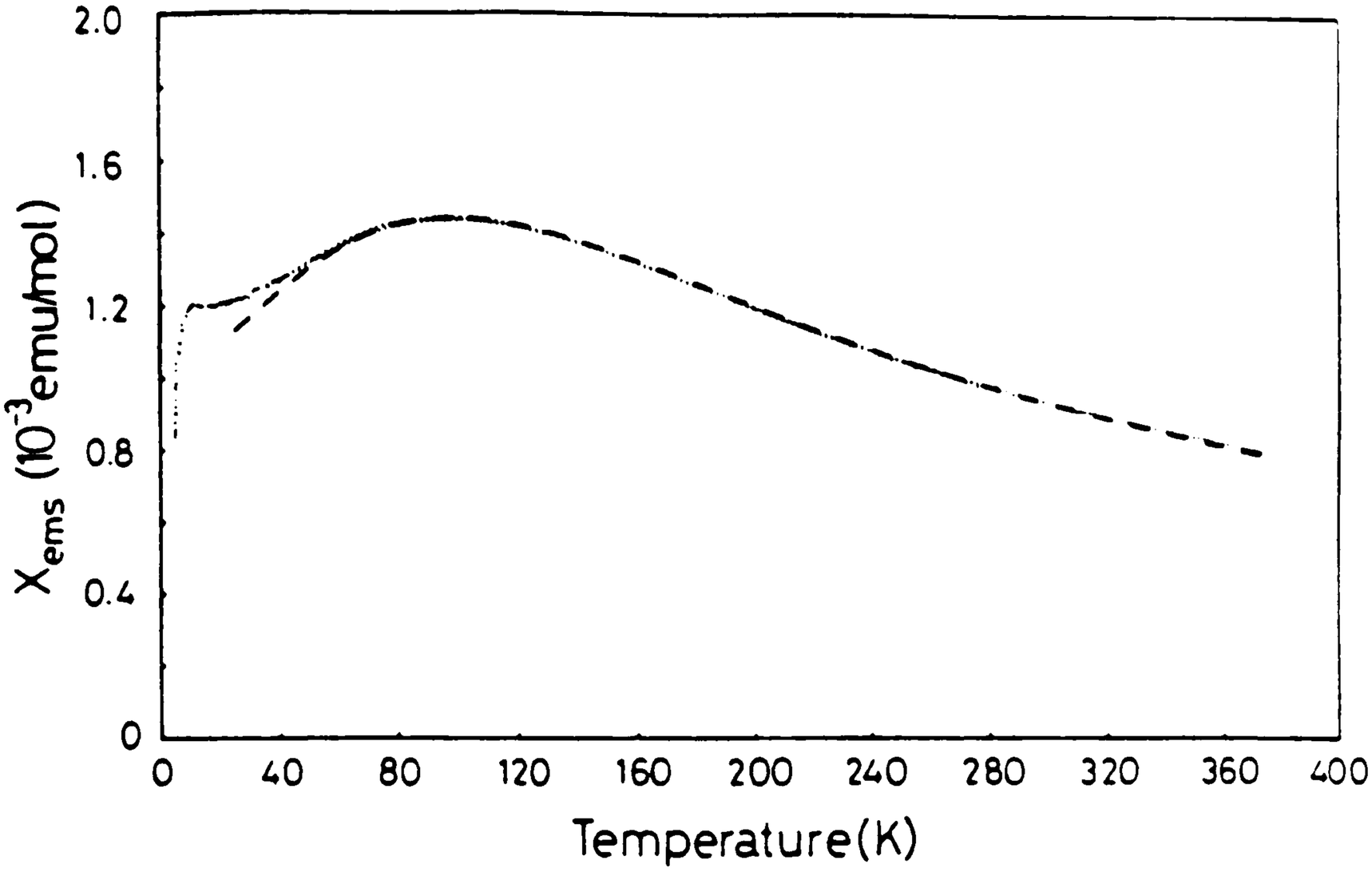

Figure 5.3: *Magnetic susceptibility of MDT(TCNQ)$_2$ (205) as a function of temperature. The dashed curve is the calculated Bonner-Fischer susceptibility fit.*

Above 40K, the data are well fitted by a Bonner-Fischer susceptibility[177]. Such a susceptibility variation is characteristic of a strongly dimerised TCNQ chain, with complete localisation of charge - in the case of salt (205), this corresponds to a spin of $\frac{1}{2}$ on each TCNQ dimer, as deduced from X-ray analysis. The transition at 5.5K may be due to a spin-Peierls transition leading to a non-magnetic ground-state, analogous to the 20K transition in MEM(TCNQ)$_2$[172]. The effect of a spin-Peierls transition in salt (205), as in MEM(TCNQ)$_2$, would be to cause tetramerisation of the TCNQ chains. Unfortunately, the transition in salt (205) occurs at the limit of our experiment, which has precluded any useful analysis of the data in terms of a spin-Peierls transition. MEM(TCNQ)$_2$ shows a phase transition at about 335K, above which the conductivity is metallic and the TCNQ chains are almost regular[172]; MDT(TCNQ)$_2$ remains dimerised to 380K, as judged by magnetic susceptibility measurements.

5.7 CONCLUSION

Three sulphonium salts of TCNQ, (205)-(207), have been studied and shown to be semiconducting. Structural analysis of MDT(TCNQ)$_2$ (205) shows the TCNQ chains to be dimerised by virtue of an unusual slipped stacking, which is particularly prominent between dimers. The FT-IR and UV-visible spectra of salts (205)-(207) are strikingly similar, suggesting similar structures for salts (205)-(207). However, the magnetic behaviour of salt (205) is dramatically different from salts (206) and (207). In particular, a sharp transition at 5.5K in the magnetic susceptibility of salt (205) is found, which may be due to a spin-Peierls transition to a non-magnetic ground state. With this in mind, it appears that no direct analogies can be safely drawn, between the known structure of MDT(TCNQ)$_2$ (205) and those of salts (206) and (207).

In conclusion, we have have demonstrated that the previously unstudied cationic saturated sulphur heterocycles offer considerable potential in the area of novel, conducting organic molecules.

CHAPTER SIX

EXPERIMENTAL

6.1 GENERAL METHODS

Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 577 and 547 spectrophotometers; samples were either embedded in KBr discs, or Nujol mulls (neat, if liquids) between KBr plates, as indicated. Fourier-transform infrared spectra were recorded on a Mattson-Sirius 100 fourier-transform instrument, with samples embedded in KBr discs. Solution-state ultra-violet spectra were recorded on a Kontron Uvikon 930 instrument, with solvents as indicated. UV-visible-near-IR spectra were obtained on a Cary 2300 spectrophotometer; samples were Nujol mulls on CaF_2 plates.

Proton NMR and carbon-13 NMR spectra were recorded on a Bruker AC 250 instrument, operating at 250.134 MHz for protons and 62.896 MHz for the carbon nucleus. Chemical shifts, given in ppm, are relative to tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on a VG 7070E instrument, operating at 70eV, with ionisation modes as indicated. High resolution masses were measured in the EI mode. All selenium-containing mass peaks are reported for ^{80}Se. Elemental analyses were performed on either a Carlo-Erba Strumentazione (C,H,N) or Perkin-Elmer HGA 500 (S).

TLC data were obtained using Merck pre-coated alumina (0.2 mm) or Merck pre-coated silica (0.2 mm) aluminium backed sheets. For column chromatography, Merck alumina (activity II to III, 70-230 mesh) or Merck silica gel (70-230 mesh) were employed as indicated. Neutral alumina refers to alumina pre-soaked in ethyl acetate for 24h. All solvents were distilled prior to use in chromatography.

Solvents were dried from the following agents under a nitrogen atmosphere: diethyl ether and THF (sodium metal then $LiAlH_4$): benzene

and toluene (sodium metal); chlorocarbons (P_2O_5): acetonitrile (CaH_2): methanol (magnesium methoxide) and ethanol (magnesium ethoxide). All other reagents were reagent grade and used as supplied, unless otherwise stated.

Cyclic voltammetry (CV) experiments were performed in a one-compartment cell with platinum working and counter electrodes and a silver/silver chloride reference electrode. Measurements were made with a BAS 100 electrochemical analyser and were i.r. compensated. The cell contained a solution of donor (~ 1 x 10^{-5} M) with oven-dried (120^{o}C) tetrabutylammonium perchlorate (TBAP) (0.01 M) as supporting electrolyte in dry acetonitrile (*ca.* 10 ml); all solutions were purged with argon and retained under the inert atmosphere while the CV data were recorded.

Bulk magnetic susceptibility data were obtained using a Faraday balance by either Dr. G.J. Ashwell (Cranfield) or Dr. R.H. Friend (Cambridge).

Conductivity measurements on powdered samples were obtained using the two-probe technique; samples were manually compressed between two steel probes and the sample resistance monitored with a Fluka 8000A Digital Multimeter. Variable temperature (300-77 K) single crystal conductivity measurements were obtained using standard four-probe techniques; four contacts were made using air-drying silver paste and a Keithley 228 voltage/current source was used. Conductivity measurements on LB films were performed using the two-probe technique; contacts on the film were made with air-drying silver paste. A Keithley 414A Current Source and a Time Electronics 2003S Voltage Source were used to monitor the resistance.

6.2 EXPERIMENTAL TO CHAPTER 2

6.2.1 Materials

1,4-Di(bromomethyl)naphthalene (83) was prepared according to the literature procedure from 1,4-dimethylnaphthalene, N-bromosuccinamide and AIBN in carbon tetrachloride (64% yield). Mpt. 188-191°C (lit.[115] 188°C).

9,10-Di(chloromethyl)anthracene (86) was prepared following the literature procedure from anthracene, formalin and hydrogen chloride in dioxan (62% yield). Mpt. 255-261°C (lit.[117] 258-260°C).

4,4'-Di(chloromethyl)biphenyl (89) was kindly supplied by Seal Sands Chemicals Limited.

1,3-Dithiolium tetrafluoroborate (113, X = BF_4^-) was prepared in three steps following the literature procedure from 1,3-dithiole-2-thione (111)[127], (88% yield). Mpt. 128-130°C; δ_H (CF_3CO_2H): 11.38 (1H, s) and 9.35 (2H,s) ppm [lit.[129] Mpt. not given; δ_H (CF_3CO_2H): 11.43 (1H,s) and 9.45 (2H,s) ppm].

4,5-Dimethyl-1,3-dithiolium tetrafluoroborate (114, X = BF_4^-) was prepared analogously to cation (113) from 4,5-dimethyl-1,3-dithiole-2-thione (112)[21], (85% yield). Mpt. 125-126°C (lit.[109b] 123-125°C).

6.2.2.1 1,4-Naphthalene-bis(dithiocarboxylate)dipiperidinium salt (84)

This material is representative of the bis(dithiocarboxylates) prepared. A mixture of elemental sulphur (3.8g, 0.12 mol) and sodium methoxide [from sodium (2.8g, 0.12 mol)] in dry methanol (250 ml) was refluxed for 2h under nitrogen with mechanical stirring. Compound (83) (10g, 0.03 mol) was added dropwise as a suspension in dry methanol

(25 ml) to the refluxing mixture over a period of 2h. After refluxing for a further 15h, the mixture was cooled, the solvent evaporated *in vacuo*, the residue dissolved in water (100 ml), filtered and acidified with dilute hydrochloric acid (2M, 30 ml) to yield the bis(dithiocarboxylic acid) as a pungent deep-red precipitate. Dichloromethane was added until all the precipitate had dissolved (*ca.* 120 ml), the mixture was extracted into dichloromethane (3 x 50 ml), the combined extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo* to ~ 50 ml volume. After cooling to -5°C, piperidine (*ca.* 9ml, 0.09 mol) was added dropwise until precipitation was complete. The solid was collected by filtration, washed with ether (3 x 50 ml) and dried *in vacuo* to afford the **dipiperidinium salt (84)** (7.8g, 55%) as an orange powder. Mpt. 154-155°C (dec); Analysis found: C, 58.4; H, 6.4; N, 5.9; S, 28.1; Required for $C_{22}H_{30}N_2S_4$: C, 58.6; H, 6.7; N, 6.2; S, 28.5%; ν_{max} (Nujol): 2940, 2830, 1595, 1510, 1460, 1035, 1012, 950, 865 cm^{-1}.

6.2.2.2 9,10-Anthracene-bis(dithiocarboxylate)dipiperidinium salt (87)

Following the procedure described for salt (84) (Chapter 6.2.2.1), elemental sulphur (7g, 0.22 mol), sodium methoxide [from sodium (5g, 0.22 mol)] and compound (86) (15g, 0.055 mol) were refluxed in dry methanol (400 ml) for 72h. After workup, the **dipiperidinium salt (87)** (21.8g, 79%) was isolated as an orange solid. Mpt. 111-113°C (dec); Analysis found: C, 62.1; H, 6.0; N, 5.6; Required for $C_{26}H_{32}N_2S_4$: C, 62.4; H, 6.4; N, 5.6%; ν_{max} (Nujol): 2935, 2832, 1590, 1510, 1465, 1040, 1000, 955, 840 cm^{-1}.

6.2.2.3 4,4'-Biphenyl-bis(dithiocarboxylate)dipiperidinium salt (90)

Following the procedure described for salt (84) (Chapter 6.2.2.1), elemental sulphur (3.8g, 0.12 mol), sodium methoxide [from sodium (2.8g, 0.12 mol)] and compound (89) (7.5g, 0.03 mol) were refluxed in dry methanol (150 ml) for 16h. Workup afforded the **dipiperidinium salt (90)** (11.5g, 80%) as an orange solid. Mpt. 161-163^{o}C; Analysis found: C, 60.2; H, 6.9; N, 5.7; Required for $C_{24}H_{32}N_2S_4$: C, 60.5; H, 6.8; N, 5.9%; ν_{max} (Nujol): 2940, 2860, 2840, 1585, 1510, 1500, 1475, 1465, 1035, 1000, 955, 840 cm^{-1}.

6.2.3.1 1,4-Bis(2-oxo-1-methylpropyldithiocarboxy)naphthalene (85)

This material is representative of the bis(dithioesters) prepared. A solution of 3-chloro-2-butanone (2.2g, 0.02 mol) in dry dichloromethane (20 ml) was added dropwise over 0.5h to a stirred suspension of salt (84) (4.5g, 0.01 mol) in dry dichloromethane (100 ml) under nitrogen at 20^{o}C. The mixture was stirred for 12h, and the solvent evaporated *in vacuo*. Column chromatography (silica, 8 x 4 cm) of the residue, eluting with cyclohexane-dichloromethane (1:1 v/v), yielded **compound (85)** (2.7g, 63%) as a bright red solid. Mpt. 150-153^{o}C; Analysis found: C, 57.3; H, 5.0; Required for $C_{20}H_{20}O_2S_4$: C, 57.1; H, 4.8%; m/e EI: 420 (M^+), CI: 421; ν_{max} (Nujol): 2940, 1700, 1445, 1372, 1358, 1230(b), 1035, 920 cm^{-1}; δ_H ($CDCl_3$): 7.98 (2H,s), 8.21 and 7.72 (each 2H,AA'XX'), 4.91 (2H,q,J=6Hz), 2.33 (6H,s), 1.60 (6H,d,J=6Hz) ppm.

6.2.3.2 9,10-Bis(2-oxo-1-methylpropyldithiocarboxy)anthracene (88)

Following the procedure described for compound (85) (Chapter 6.2.3.1), a mixture of salt (87) (15g, 0.03 mol) and 3-chloro-2-butanone (6.5g, 0.06 mol) was stirred in dry dichloromethane (120 ml) for 14h to afford **compound (88)** (10.6g, 62%) as red crystals. Mpt. 172-174^{o}C; Analysis found: C, 60.9; H, 4.9; Required for $C_{24}H_{22}O_2S_4$: C, 61.2: H. 4.7%; m/e EI: 470 (M^+), CI: 471; ν_{max} (Nujol): 2920, 1705, 1440, 1350, 1238, 1162, 1150, 1090, 1015, 950, 760 cm^{-1}; δ_H ($CDCl_3$): 7.81 and 7.35 (each 4H,AA'XX'), 4.89 (2H,q,J=7Hz), 2.34 (6H,s), 1.71 (6H,d,J=7Hz) ppm.

6.2.3.3 4,4'-Bis(2-oxo-1-methylpropyldithiocarboxy)biphenyl (91)

Following the procedure described for compound (85) (Chapter 6.2.3.1), a mixture of salt (90) (4.8g, 0.01 mol) and 3-chloro-2-butanone (2.2g, 0.02 mol) in dry dichloromethane (75 ml) was stirred for 14h to afford **compound (91)** (3.4g, 75%) as a red powder. Mpt. 163-167^{o}C; Analysis found: C, 59.1; H, 4.9; Required for $C_{22}H_{22}O_2S_4$: C, 59.2; H, 5.0%; m/e EI: 446 (M^+), CI: 447; ν_{max} (Nujol): 2935, 1710, 1445, 1370, 1345, 1235(b), 1145, 1090, 940 cm^{-1}; δ_H ($CDCl_3$): 8.04 and 7.65 (each 4H,AX J=8Hz), 4.89 (2H,q,J=7Hz), 2.31 (6H,s), 1.57 (6H,d,J=7Hz) ppm.

6.2.4.1 1,4-Naphthalene-2,2'-bis(4,5-dimethyl-1,3-dithiolium) dication salt (80)

This material is representative of the bis(dithiolium) dication salts prepared. Compound (85) (2.5g, 6 mmol) was added in portions to stirring sulphuric acid (conc., 5 ml) at -10^{o}C, the reaction temperature being maintained below -5^{o}C at all times. The solution was stirred for

2.5h at -10°C and then allowed to warm slowly to 20°C over a period of 1h. Dilution with ethyl acetate (15 ml) precipitated a solid, which was collected by filtration, washed with ice-cold acetone (3 x 10 ml) and dried *in vacuo* to afford the **di(hydrogensulphate) salt (80a)** (3.3g, 92%) as a brown powder. Analysis found: C, 43.6; H, 2.7; Required for $C_{20}H_{20}O_8S_6$: C, 41.4; H, 3.5%; ν_{max} (Nujol): 1510, 1370, 1310, 1170, 1020, 860, 775, 730 cm^{-1}.

Dication salt (80a) was found to be impure by elemental analysis, but could be conveniently purified by conversion to its corresponding **bis-(hexafluorophosphate) salt (80b)** using the following method: Hexafluorophosphoric acid (60%, 5 ml) was added dropwise to a stirred solution of the di(hydrogensulphate) salt (80a) (2.5g, 4.5 mmol) in water (5 ml) at 20°C. The resultant precipitate was collected by filtration, washed with ice-cold acetone (3 x 15 ml) and dried *in vacuo* to yield **bis(hexafluorophosphate) salt (80b)** (2.7g, 88%) as a golden-yellow powder. Mpt. 170°C (dec); Analysis found: C, 35.6; H, 2.7; S, 19.2; Required for $C_{20}H_{18}F_{12}P_2S_4$: C, 35.5; H, 2.7; S, 19.0%; m/e FAB (glycerol): 193 (M^{2+}), 145 (PF_6^-); δ_H (CF_3CO_2H): 8.31 and 7.99 (each 2H,AA'XX'), 8.13 (2H,s), 2.97 (12H,s) ppm.

6.2.4.2 9,10-Anthracene-2,2'-bis(4,5-dimethyl-1,3-dithiolium) dication salt (81)

The di(hydrogensulphate) salt (81) was prepared analogously to salt (80a) (Chapter 6.2.4.1). Compound (88) (2.3g, 5 mmol) in sulphuric acid (conc., 5 ml) for 4h afforded **salt (81)** (2.7g, 86%) as a brown powder. Mpt. *ca.* 160°C (dec); Analysis found: C, 46.0; H, 3.3; S, 29.1; Required for $C_{24}H_{22}O_8S_6$: C, 45.7; H, 3.5; S, 30.5%; ν_{max} (Nujol): 1515, 1350,

1345, 1335, 1300, 1170, 1005, 860, 830, 790 cm^{-1}; δ_H (CF_3CO_2H): 8.46 and 8.02 (each 4H,AA'XX'), 3.01 (12H,s) ppm. Di(hydrogensulphate) salt (81) proved to be too insoluble for further purification by conversion to any other anion salt.

6.2.4.3 4,4'-Biphenyl-2,2'-bis(4,5-dimethyl-1,3-dithiolium) dication salt (82)

The di(hydrogensulphate) salt (82a) was prepared analogously to salt (80a) (Chapter 6.2.4.1). Compound (91) (1.3g, 3 mmol) in sulphuric acid (conc., 5 ml) for 2h yielded **salt (82a)** (1.6g, 90%) as a yellow-brown powder. Analysis found: C, 45.1; H, 2.9; Required for $C_{22}H_{22}O_8S_6$: C, 43.5; H, 3.7%; ν_{max} (Nujol): 1505, 1370, 1340, 1325, 1315, 1150, 1020, 800 cm^{-1}.

Di(hydrogensulphate) salt (82a) did not give satisfactory elemental analysis, but could be easily purified by conversion to its corresponding **bis(hexafluorophosphate) salt (82b)** following the procedure described for salt (80b). Salt (82a) (1g, 1.6 mmol) and hexafluorophosphoric acid (60%, 3 ml) in water (5 ml) afforded **dication salt (82b)** (0.95g, 85%) as a golden-yellow powder. Mpt. *ca.* 220°C (dec): Analysis found: C, 37.4; H, 3.1; S, 18.6; Required for $C_{22}H_{20}F_{12}P_2S_4$: C, 37.6; H, 2.9; S, 18.3%; m/e FAB (glycerol): 206 (M^{2+}), 145 (PF_6^-); δ_H (CF_3CO_2H): 8.51 and 8.08 (each 4H,AX J=8Hz), 2.93 (12H,s) ppm.

6.2.5 1,4-Naphthalene-2,2'-bis(4,5-dimethyl-1,3-dithiole) (94)

Sodium borohydride (115 mg, 3 mmol) was added in portions over 0.5h to a stirred suspension of salt (80b) (500 mg, 0.7 mmol) in dry ethanol (25 ml) at 20°C. After a further 2h at 20°C, the solvent was evaporated *in vacuo*, the residue dissolved in dichloromethane (25 ml), filtered and the solvent again evaporated *in vacuo*. Column chromatography (silica, 5 x 1 cm) of the residue, eluting with dichloromethane, gave **compound (94)** (165 mg, 58%) as a red-brown solid. Mpt. >240°C; Analysis found: C, 62.0; H, 4.9; Required for $C_{20}H_{20}S_4$: C, 61.8; H, 5.2%; m/e EI: 388 (M^+), CI: 389; ν_{max} (Nujol): 1595, 1535, 1515, 1370, 1275, 1100, 965, 940, 760, 745, 665 cm^{-1}; δ_H ($CDCl_3$): 8.00 (2H,s), 7.96 and 7.55 (each 2H, AA'XX'), 6.48 (2H,s), 1.90 (12H,s) ppm.

6.2.6 1,4-Naphthalene-2-(4,5-dimethyl-1,3-dithiole)-2'-(4,5-dimethyl-1,3-dithiolium) hexachloroantimonate salt (95)

A stirred solution of compound (94) (200 mg, 0.5 mmol) and triphenylcarbeniumhexachloroantimonate (580 mg, 1.0 mmol) in dry dichloromethane (30 ml) under nitrogen was refluxed for 3h. After the solution had cooled, ether (20 ml) was added and the solid collected by filtration, washed with ether (3 x 10 ml) and dried *in vacuo* to afford **salt (95)** (270 mg, 75%) as a brown powder. Mpt. >240°C; Analysis found: C, 29.7; H, 2.3; Required for $C_{20}H_{19}Cl_6S_4Sb$: C, 33.2; H, 2.7%; m/e FAB (glycerol): 387 (M^+); δ_H (CF_3CO_2H): 8.43-7.51 (6H,m), 5.81 (1H,s), 2.73 (6H,s), 1.91 (6H,s) ppm.

6.2.7 1,4-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-1,4-dihydronaphthalene-2,3-dichloro-5,6-dicyanoquinodimethane complex (1:1 stoichiometry) (96)

A stirred solution of compound (94) (200 mg, 0.5 mmol) and DDQ (230 mg, 1.0 mmol) in dry benzene (10 ml) was refluxed for 2h under nitrogen. The solution was cooled and the solid collected by filtration, washed with ether (3 x 10 ml) and dried *in vacuo*. The resultant brown powder was identified as **complex (96)** (70 mg, 20%). Mpt. 85-90^{o}C (dec); Analysis found: C, 54.9; H, 2.9; N, 4.7; Required for $C_{28}H_{18}N_2O_2Cl_2S_4$ (*ie.* a 1:1 complex): C, 54.8; H, 3.0; N, 4.6%; ν_{max} (KBr,FT-IR): 3400-3000 (br), 2222, 1566, 1500, 1450, 1199, 1064, 1012, 973, 862, 688 cm^{-1}; λ_{max} (MeCN): 780, 640, 415, 350, 260, 210 nm.

6.2.8 1,4-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-1,4-dihydronaphthalene-iodine complex (1:2.8 stoichiometry) (97)

Dication salt (80b) (75 mg, 0.1 mmol) was added to a solution of lithium iodide (67 mg, 0.5 mmol) in acetone (15 ml) and the resultant solution heated under reflux for 0.5h. The solution was cooled, the solid collected by filtration, washed with ice-cold acetone (3 x 10 ml) and dried in air to afford **complex (97)** (70 mg, 95%) as a red powder. Mpt. 245^{o}C (dec); Analysis found: C, 32.5; H, 2.4; S, 17.3; Required for $C_{20}H_{18}S_4I_{2.8}$ (*ie.* a 1:2.8 complex): C, 32.4; H, 2.4; S, 17.3%. The analysis of salt (97) was unchanged after two recrystallisations from acetone.

6.2.9.1 1,4-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-1,4-dihydronaphthalene-7,7,8,8-tetracyano-p-quinodimethane complex (1 : 2.4 stoichiometry) (98)

Dication salt (80b) (75 mg, 0.1 mmol) in acetonitrile (5 ml) was added to a solution of $Li^{+}TCNQ^{-}$ (63 mg, 0.3 mmol) in acetonitrile-acetone (1:1 v/v) (20 ml) and the resultant mixture heated under reflux for 0.5h. The solution was cooled to 20°C, the precipitate collected by filtration, washed with acetone (2 x 5 ml) and dried in air to afford **complex (98)** (51 mg, 52%) as a black powder. Mpt. 168°C (dec); Analysis found: C, 66.9; H, 3.2; N, 15.4; Required for $C_{48.8}H_{27.6}N_{9.6}S_4$ (*ie.* a 1 : 2.4 complex): C, 66.9; H, 3.2; N, 15.3%; ν_{max} (KBr,FT-IR): 3400-3000 (br), 2197, 2177, 2154, 1559, 1540, 1521, 1506, 1294, 1090 cm^{-1}; λ_{max} (MeCN): 845, 745, 395, 200 nm; λ_{max} (Nujol): 880, 835, 780, 380 nm; ESR (powder): g = 2.0003 (singlet).

Numerous reactions using a variety of cation : TCNQ ratios afforded the same complex, as judged by elemental analysis and spectra; the best yields were obtained from the procedure detailed above.

6.2.9.2 4,4'-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-4,4'-dihydrobiphenyl-7,7,8,8-tetracyano-p-quinodimethane complex (1:2 stoichiometry) (99)

Complex (99) was prepared in exactly the same manner as complex (98) (Chapter 6.2.9.1). Metathetical reaction of dication (82b) (75 mg, 0.1 mmol) and $Li^{+}TCNQ^{-}$ (42 mg, 0.2 mmol) in acetonitrile-acetone (1:1 v/v) gave **complex (98)** (20 mg, 25%) as a black powder. Mpt. >250°C; Analysis found: C, 67.5; H, 3.2; N, 13.1; Required for $C_{46}H_{28}N_8S_4$ (*ie.*

a 1:2 complex): C, 67.3; H, 3.4; N, 13.7%; ν_{max} (KBr,FT-IR): 3450-3000 (vbr), 2183, 2169, 2151, 1560, 1512, 1331, 1154 cm^{-1}; λ_{max} (MeCN): 845. 745, 395, 200 nm; λ_{max} (Nujol): 895, 835, 780, 385 nm.

6.2.10.1 2-Dimethoxyphosphinyl-1,3-dithiole (100)

Freshly-distilled trimethylphosphite (0.62 ml, 5.3 mmol) and sodium iodide (0.8g, 5.3 mmol) were added successively to a stirred solution of cation (113) (1.0g, 5.3 mmol) in dry acetonitrile (50 ml) under a nitrogen atmosphere at 20°C. A slightly exothermic reaction immediately took place. Stirring was continued for 2h, whereupon the solvent was evaporated *in vacuo*. Water (25 ml) was added to the residue and the mixture extracted into dichloromethane (3 x 25 ml). The combined extracts were dried ($MgSO_4$), filtered and the solvent evaporated *in vacuo*. The residue was chromatographed (neutral alumina column, 6 x 2 cm), eluting with ethyl acetate, to afford **ester (100)** (1.05g, 95%) as a deep red hygroscopic oil. Analysis found: C, 28.0; H, 4.5; Required for $C_5H_9O_3PS_2$: C, 28.3; H, 4.3%; m/e EI: 212 (M^+); ν_{max} (neat): 3015, 2950, 2920, 2850, 1665, 1570, 1300, 1250(br), 1040(br), 910, 890 cm^{-1}; δ_H ($CDCl_3$): 5.98 (2H,s), 4.73 (1H,d,J=4.5Hz), 3.75 (6H,d,J=10.5Hz) ppm.

6.2.10.2 4,5-Dimethyl-2-dimethoxyphosphinyl-1,3-dithiole (101)

Following the procedure detailed above for ester (100) (Chapter 6.2.10.1), freshly-distilled trimethylphosphite (0.6 ml, 4.8 mmol), sodium iodide (0.72g, 4.8 mmol) and cation (114) (1.05g, 4.8 mmol) were stirred together in dry acetonitrile (50 ml) under nitrogen for 2h. Column chromatography (neutral alumina, 6 x 2 cm), eluting with ethyl acetate, afforded **ester (101)** (1.1g, 95%) as a deep red hygroscopic oil.

Analysis found: C, 35.3; H, 5.4; Required for $C_7H_{13}O_3PS_2$: C, 35.0: H. 5.5%; m/e EI: 240 (M^+); ν_{max} (neat): 3005, 2960, 2940, 2860, 1675, 1585, 1305, 1250(br), 1170, 1040(br), 910, 870, 770, 680 cm^{-1}; δ_H ($CDCl_3$): 4.75 (1H,d,J=4.5Hz), 3.80 (6H,d,J=10.4Hz), 1.86 (2H,s) ppm.

6.2.11 Wittig-Horner Reactions of 2-Dimethoxyphosphinyl-1,3-dithiole (100) and 4,5-Dimethyl-2-dimethoxyphosphinyl-1,3-dithiole (101)

6.2.11.1 General Procedure

In all cases, glassware was rigorously oven- and flame-dried. n-Butyl lithium (n-BuLi) (1.6 M in hexane, 1.1 mol equivalent) was syringed into a stirred solution of ester (100), or ester (101) (1 mol equivalent) in dry THF at -78°C under nitrogen; reaction occurred immediately with a concomitant colour change from red to yellow. After 0.5h at -78°C, the carbonyl compound in dry THF was syringed into the solution of phosphonate carbanion (120), or (121), respectively. The mixture was stirred for 1h at -78°C, and then allowed to warm to 20°C overnight. The THF was evaporated *in vacuo*, water (75 ml) added and the residue extracted with dichloromethane (3 x 75 ml). The combined extracts were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Column chromatography on silica, with eluents as indicated, afforded the expected products. Further purification, if necessary, could be achieved by recrystallisation from ethanol, dichloromethane-hexane (1:1 v/v) or dichloromethane-methanol (1:1 v/v).

6.2.11.2 2-Cyclopentylidene-1,3-dithiole (122)

Cyclopentanone (0.095 ml, 1.05 mmol) in dry THF (5 ml) was added to a solution of carbanion (120) [from ester (100) (220 mg, 1.05 mmol) and n-BuLi (1.6 M, 0.72 ml, 1.15 mmol)] in dry THF (50 ml) at -78^{o}C. Column chromatography (silica, 15 x 1 cm), eluting with dichloromethane-hexane (1:1 v/v), afforded **compound (122)** (115 mg, 65%) as a light yellow solid. Mpt. 45-47^{o}C; Analysis found: C, 56.1; H, 6.1; S, 38.0; Required for $C_8H_{10}S_2$: C, 56.4; H, 5.9; S, 37.7%; m/e EI: 170 (M^+), CI: 171; ν_{max} (Nujol): 1580, 1535, 1270, 1130, 830, 760, 740 cm^{-1}; δ_H ($CDCl_3$): 6.21 (2H,s), 2.57-2.39 (4H,m), 1.68-1.51 (4H,m) ppm.

6.2.11.3 4,5-Dimethyl-2-cyclopentylidene-1,3-dithiole (124)

Cyclopentanone (0.1 ml, 1.15 mmol) in dry THF (5 ml) was added to a solution of carbanion (121) [from ester (101) (275 mg, 1.15 mmol) and n-BuLi (1.6 M, 0.79 ml, 1.25 mmol)] in dry THF (50 ml) at -78^{o}C. Column chromatography (silica, 15 x 1 cm), eluting with dichloromethane-hexane (1:1 v/v), afforded **compound (124)** (164 mg, 72%) as a yellow solid. Mpt. 44-45^{o}C; Analysis found: C, 60.4; H, 6.9; Required for $C_{10}H_{14}S_2$: C, 60.6; H, 7.1%; m/e EI: 198 (M^+), CI: 199; ν_{max} (Nujol): 1590, 1530, 1270, 1235, 1220, 820, 750 cm^{-1}; δ_H ($CDCl_3$): 2.51-2.36 (4H,m), 1.90 (6H,s), 1.61-1.49 (4H,m) ppm.

6.2.11.4 2-(Diphenylmethylene)-1,3-dithiole (123)

Benzophenone (190 mg, 1.05 mmol) in dry THF (5 ml) was added to a solution of carbanion (120) [from ester (100) (220 mg, 1.05 mmol) and n-BuLi (1.6 M, 0.72 ml, 1.15 mmol)] in dry THF (50 ml) at -78^{o}C. Column

chromatography (silica, 15 x 1 cm), eluting with toluene, afforded **compound (123)** (190 mg, 68%) as a yellow solid. Mpt. 85-86°C; Analysis found: C, 71.7; H, 4.2; Required for $C_{16}H_{12}S_2$: C, 71.6; H, 4.5%; m/e EI: 268 (M^+), CI: 269; ν_{max} (Nujol): 1595, 1510, 1270, 1135, 1030, 950, 830, 760, 755, 700 cm^{-1}; δ_H ($CDCl_3$): 7.37-7.14 (10H,m), 6.29 (2H,s) ppm.

6.2.11.5 4,5-Dimethyl-2-(diphenylmethylene)-1,3-dithiole (125)

Benzophenone (210 mg, 1.15 mmol) in dry THF (5 ml) was added to a solution of carbanion (121) [from ester (101) (275 mg, 1.15 mmol) and n-BuLi (1.6 M, 0.72 ml, 1.25 mmol)] in dry THF (50 ml) at -78°C. Column chromatography (silica, 15 x 1 cm), eluting with toluene, afforded **compound (125)** (210 mg, 62%) as a yellow solid. Mpt. 88-90°C; Analysis found: C, 72.8; H, 5.5; Required for $C_{18}H_{16}S_2$: C, 73.0; H, 5.4%; m/e EI: 296 (M^+), CI: 297; ν_{max} (Nujol): 1580, 1500, 1200, 980, 820, 770, 690 cm^{-1}; δ_H ($CDCl_3$): 7.31-7.09 (10H,m), 1.87 (6H,s) ppm.

6.2.11.6 9,10-Bis(1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (126)

A suspension of anthraquinone (310 mg, 1.5 mmol) in dry THF (15 ml) was added to a solution of carbanion (120) [from ester (100) (635 mg, 3 mmol) and n-BuLi (1.6 M, 2.05 ml, 3.3 mmol)] in dry THF (100 ml) at -78°C. Column chromatography (silica, 30 x 2 cm), eluting with cyclohexane-toluene (3:1 v/v), afforded **compound (126)** (350 mg, 62%) as an orange solid. Mpt. >240°C; Analysis found: C, 63.2; H, 3.0; S, 34.0; Required for $C_{20}H_{12}S_4$: C, 63.1; H, 3.2; S, 33.7%; m/e EI: 380 (M^+), CI: 381; ν_{max} (Nujol): 3030, 1595, 1535, 1515, 1370, 1280, 1090, 970, 940, 775, 755, 740, 670 cm^{-1}; λ_{max} (MeCN): 415, 323, 273, 253, 206 nm; δ_H ($CDCl_3$): 7.69 and 7.28 (each 2H,first order AA'XX'), 6.30 (4H,s) ppm.

Continued elution of the column with dichloromethane yielded unreacted anthraquinone (60 mg, 20%), followed by a second product. Further purification of this fraction by preparative TLC (silica plate, 25 x 25 cm), eluting with dichloromethane-hexane (1:1 v/v), followed by recrystallisation from dichloromethane afforded an analytically pure sample of **9-oxo-10-(1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (132)** (45 mg, 10%), as a bright orange solid. Mpt. 219-221^{o}C; Analysis found: C, 69.0; H, 3.6; S, 22.2; Required for $C_{17}H_{10}OS_2$: C, 69.3; H, 3.4: S, 21.8%; m/e EI: 294 (M^+), CI: 295; ν_{max} (Nujol): 2940, 2860, 1635, 1590, 1330, 1305, 1290, 1265, 1165, 935, 760, 720, 680 cm^{-1}; λ_{max} (MeCN): 467, 360, 246, 192 nm; δ_H ($CDCl_3$): 8.27, 7.95, 7.66 and 7.45 (each 2H,first order AMRX, all ortho J_{HH}=8Hz), 6.48 (2H,s) ppm.

6.2.11.7 9,10-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (127)

A suspension of anthraquinone (520 mg, 2.5 mmol) in dry THF (20 ml) was added to a solution of carbanion (121) [from ester (101) (1.2g, 5 mmol) and n-BuLi (1.6 M, 3.4 ml, 5.5 mmol)] in dry THF (100 ml) at -78^{o}C. Column chromatography (silica, 30 x 2 cm), eluting with cyclohexane-toluene (4:1 v/v), afforded **compound (127)** (742 mg, 68%) as an orange solid. Mpt. >240^{o}C; Analysis found: C, 65.9; H, 4.6; S, 29.5; Required for $C_{24}H_{20}S_4$: C, 66.0; H, 4.6; S, 29.4%; m/e EI: 436 (M^+), CI: 437; ν_{max} (Nujol): 1590, 1575, 1540, 1520, 1510, 1275, 1150, 1085, 960, 860, 775, 745, 660 cm^{-1}; λ_{max} (MeCN): 433, 369, 235, 206 nm; δ_H ($CDCl_3$): 7.62 and 7.25 (each 4H,first order AA'XX'), 1.91 (12H,s) ppm.

Continued elution with dichloromethane yielded unreacted anthraquinone (80 mg, 15%), followed by a second product, which was purified by preparative TLC (silica plate, 25 x 25 cm), eluting with cyclohexane-dichloromethane (2:1 v/v), followed by recrystallisation from dichloromethane to yield an analytically pure sample of **9-oxo-10-(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (133)** (96 mg, 12%) as an orange solid. Mpt. 217-218^{o}C; Analysis found: C, 71.0; H, 4.5; S, 20.1; Required for $C_{19}H_{14}OS_2$: C, 70.8; H, 4.4; S, 19.9%; m/e EI: 322 (M^+). CI: 323; ν_{max} (Nujol): 2940, 2860, 1645, 1595, 1335, 1310, 1300, 1170, 765, 685 cm^{-1}; λ_{max} (MeCN): 481, 370, 272, 247, 194 nm; δ_H ($CDCl_3$): 8.26, 7.89, 7.62 and 7.39 (each 2H,first order AMRX, all ortho J_{HH}=8Hz), 1.98 (6H,s) ppm.

6.2.11.8 9-(1,3-Dithiole-2-ylidene)-10-(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (136)

A solution of ketone (132) (90 mg, 0.3 mmol) in dry THF (5 ml) was added to a solution of carbanion (121) [from ester (101) (70 mg, 0.3 mmol) and n-BuLi (1.6 M, 0.2 ml, 0.33 mmol)] in dry THF (50 ml) at -78^{o}C. Column chromatography (silica, 30 x 2 cm), eluting with cyclohexane-toluene (1:1 v/v), afforded **compound (136)** (90 mg, 74%) as an orange solid. Mpt. >240^{o}C; Analysis found: C, 64.8; H, 3.9; S, 31.6; Required for $C_{22}H_{16}S_4$: C, 64.7; H, 3.9; S, 31.4%; m/e EI: 408 (M^+). CI: 409; ν_{max} (Nujol): 3030, 1585, 1545, 1535, 1510, 1275, 1095, 960, 865, 755, 740, 630 cm^{-1}; λ_{max} (MeCN): 430, 360, 235, 200 nm; δ_H ($CDCl_3$): 7.69-7.62 (4H,m), 7.28-7.25 (4H,m), 6.27 (2H,s), 1.92 (6H,s) ppm.

Alternatively, reaction of ketone (133) (95 mg, 0.3 mmol) with carbanion (120) [from ester (100) (60 mg, 0.3 mmol) and n-BuLi (1.6 M, 0.2 ml, 0.33 mmol)] in dry THF (50 ml) at -78^{o}C afforded **compound (136)**

(83 mg, 68%); spectroscopic data were identical with those described above.

6.2.11.9 ($\Delta^{9,9'[10H,10'H]}$Bianthracene)-10,10'-bis(1,3-dithiole-2-ylidene) (128)

A suspension of bianthrone (96 mg, 0.25 mmol) in dry THF (10 ml) was added to a solution of carbanion (120) [from ester (100) (105 mg, 0.5 mmol) and n-BuLi (1.6 M, 0.35 ml, 0.55 mmol)] in dry THF (50 ml) at -78^{o}C. Column chromatography (silica, 25 x 2 cm), eluting with cyclohexane-toluene (1:1 v/v), afforded **compound (128)** (57 mg, 41%) as an orange-red solid. Mpt. >240^{o}C; Analysis found: C, 72.8; H, 3.9; S, 22.7; Required for $C_{34}H_{20}S_4$: C, 73.3; H, 3.6; S, 23.1%; m/e DEI: 556 (M^+), DCI: absent; ν_{max} (Nujol): 3025, 1575, 1530, 1525, 1270, 1255, 970, 760, 755, 670 cm^{-1}; λ_{max} (MeCN): 438, 378, 235, 200 nm.

6.2.11.10 ($\Delta^{9,9'[10H,10'H]}$Bianthracene)-10,10'-bis(4,5-dimethyl-1,3-dithiole-2-ylidene) (129)

A suspension of bianthrone (96 mg, 0.25 mmol) in dry THF (10 ml) was added to a solution of carbanion (121) [from ester (101) (120 mg, 0.5 mmol) and n-BuLi (1.6 M, 0.35 ml, 0.55 mmol)] in dry THF (50 ml) at -78^{o}C. Column chromatography (silica, 20 x 2 cm), eluting with toluene-cyclohexane (1:1 v/v), afforded **compound (129)** (58 mg, 38%) as an orange-red solid. Mpt. >240^{o}C; Analysis found: C, 74.9; H, 4.3; S, 21.3; Required for $C_{38}H_{28}S_4$: C, 74.5; H, 4.6; S, 20.9%; m/e DEI: 612 (M^+), DCI: absent; ν_{max} (Nujol): 1580, 1525, 1255, 970, 790, 690 cm^{-1}; λ_{max} (MeCN): 447, 381, 240, 200 nm.

6.2.11.11 5,12-Bis(1,3-dithiole-2-ylidene)-5,12-dihydro-naphthacene (130)

A suspension of 5,12-naphthacenequinone (105 mg, 0.4 mmol) in dry THF (10 ml) was added to a solution of carbanion (120) [from ester (100) (170 mg, 0.8 mmol) and n-BuLi (1.6 M, 0.56 ml, 0.9 mmol)] in dry THF (75 ml) at -78°C. Column chromatography (silica, 30 x 2 cm), eluting with cyclohexane-toluene (4:1 v/v), afforded **compound (130)** (93 mg, 59%) as an orange solid. Mpt. >240°C; Analysis found: C, 66.6; H, 3.4; S, 30.3; Required for $C_{24}H_{14}S_4$: C, 66.9; H, 3.3; S, 29.8%; m/e DEI: 430 (M^+), DCI: 431; ν_{max} (Nujol): 3025, 1590, 1550, 1500, 1265, 1100, 870, 755, 740, 650 cm^{-1}; λ_{max} (MeCN): 417, 385, 235, 200 nm; δ_H ($CDCl_3$): 7.98 (2H,s), 7.85 and 7.49 (each 2H,first order AA'XX'), 7.68 and 7.31 (each 2H,first order AA'XX'), 6.30 (4H,s) ppm.

6.2.11.12 5,12-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-5,12-dihydro-naphthacene (131)

A suspension of 5,12-naphthacenequinone (105 mg, 0.4 mmol) in dry THF (10 ml) was added to a solution of carbanion (121) [from ester (101) (190 mg, 0.8 mmol) and n-BuLi (1.6 M, 0.56 ml, 0.9 mmol)] in dry THF (75 ml) at -78°C. Column chromatography (silica, 30 x 2 cm), eluting with cyclohexane-toluene (4:1 v/v), afforded **compound (131)** (107 mg, 55%) as an orange solid. Mpt. >240°C; Analysis found: C, 68.7; H, 4.7; S, 25.9; Required for $C_{28}H_{22}S_4$: C, 69.1; H, 4.6; S, 26.3%; m/e DEI: 486 (M^+), DCI: 487; ν_{max} (Nujol): 1595, 1535, 1500, 1270, 1095, 870, 765, 760, 745, 690 cm^{-1}; λ_{max} (MeCN): 428, 327, 230, 205 nm; δ_H ($CDCl_3$): 7.93 (2H,s), 7.82 and 7.44 (each 2H,first order AA'XX'), 7.65 and 7.28 (each 2H,first order AA'XX'), 1.92 (12H,s) ppm.

6.2.12.1 9,10-Bis(1,3-dithiole-2-ylidene)-9,10-dihydroanthracene-7,7,8,8-tetracyano-p-quinodimethane complex (1:4 stoichiometry) (126a)

A boiling solution of donor (126) (38 mg, 0.1 mmol) in dry acetonitrile (20 ml) was added to a solution of TCNQ (1) (81 mg, 0.4 mmol) in dry acetonitrile (10 ml) and the resultant dark-green solution refluxed for 0.5h under nitrogen. After slow cooling to $0^{o}C$, the solid was collected by filtration, washed with ice-cold acetonitrile (3 x 5 ml) and dried *in vacuo* to afford **complex (126a)** (49 mg, 41%) as a black powder. Mpt. $>260^{o}C$; Analysis found: C, 68.2; H, 2.5; N, 18.5; S, 10.8; Required for $C_{68}H_{28}N_{16}S_4$ (*ie.* a 1:4 complex): C, 68.2; H, 2.4; N, 18.7; S, 10.7%; ν_{max} (KBr,FT-IR): 3450-3000(br), 2185, 2155, 1559, 1508, 1294, 1090, 610 cm^{-1}; λ_{max} (MeCN): 842, 746, 395, 200 nm.

6.2.12.2 9,10-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene-7,7,8,8-tetracyano-p-quinodimethane complex (1:4 stoichiometry) (127a)

This complex was prepared in exactly the same manner as complex (126a) (Chapter 6.2.12.1). Donor (127) (44 mg, 0.1 mmol) and TCNQ (1) (81 mg, 0.4 mmol) in dry acetonitrile (30 ml) yielded **complex (127a)** (60 mg, 48%) as a black powder. Mpt. $>260^{o}C$; Analysis found: C, 68.8; H, 3.1; N, 18.2; S, 9.9; Required for $C_{72}H_{36}N_{16}S_4$ (*ie.* a 1:4 complex): C, 69.0; H, 2.9; N, 17.9; S, 10.2%; ν_{max} (KBr,FT-IR): 3450-3000(br), 2209, 2187, 2158, 1560, 1327, 1154, 1077 cm^{-1}; λ_{max} (MeCN): 843, 744, 394, 200 nm. Recrystallisation from acetonitrile gave complex (127a) as long, thin shiny needles suitable for X-ray analysis.

6.2.12.3 9,10-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene-2,5-dibromo-7,7,8,8-tetracyano-p-quinodimethane complex (1:2 stoichiometry) (127b)

This complex was prepared in exactly the same manner as complex (126a) (Chapter 6.2.12.1). Donor (127) (44 mg, 0.1 mmol) and 2,5-dibromoTCNQ (72 mg, 0.2 mmol) in dry acetonitrile (30 ml) yielded **complex (127b)** (44 mg, 38%) as a black powder. Mpt. >250^{o}C; Analysis found: C, 50.0; H, 1.9; N, 10.1; Required for $C_{48}H_{24}N_8S_4Br_4$ (*ie.* a 1:2 complex): C, 49.7; H, 2.1; N, 9.7%; ν_{max} (KBr): 2190, 1550, 1485, 1440. 1360, 1315, 1275, 1155, 1070, 990, 870, 790, 755 cm^{-1}.

6.2.12.4 9-(1,3-Dithiole-2-ylidene)-10-(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene-7,7,8,8-tetracyano-p-quinodimethane complex (1:4 stoichiometry) (136a)

This complex was prepared in exactly the same manner as complex (126a) (Chapter 6.2.12.1). Donor (136) (41 mg, 0.1 mmol) and TCNQ (1) (81 mg, 0.4 mmol) in dry acetonitrile (30 ml) yielded complex **(136a)** (39 mg, 32%) as a black powder. Mpt. ca. 250^{o}C (dec); Analysis found: C, 68.8; H, 2.7; N, 18.5; S, 10.0; Required for $C_{70}H_{32}N_{16}S_4$ (*ie.* a 1:4 complex): C, 68.6; H, 2.6; N, 18.3; S, 10.5%; ν_{max} (KBr,FT-IR): 3450-3000(br), 2180, 2158, 1563, 1497, 1081 cm^{-1}; λ_{max} (MeCN): 847, 740, 380, 195 nm.

6.2.13.1 9-Oxo-10-(1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (132)

A stirred mixture of anthrone (135) (5g, 0.025 mol) and methiodide salt (115) (8.3g, 0.03 mol) in pyridine-acetic acid (70 ml, 3:1 v/v) was refluxed for 4h. After cooling, the solvent was evaporated *in vacuo*. water (75 ml) was added and the mixture extracted with dichloromethane (3 x 75 ml). The combined extracts were washed sequentially with (i) 5% sodium carbonate solution (2 x 25 ml) and (ii) water (2 x 25 ml), dried ($MgSO_4$), filtered and the solvent evaporated *in vacuo*. Column chromatography (silica, 25 x 4 cm) of the residue, eluting with dichloromethane-hexane (2:1 v/v), afforded **ketone (132)** (6.25g, 85%). Spectroscopic data were identical with the material described previously (Chapter 6.2.11.6).

6.2.13.2 9-Oxo-10-(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (133)

Ketone (133) was prepared analogously to compound (132) (Chapter 6.2.13.1). A mixture of anthrone (135) (8.0g, 0.041 mol) and methiodide salt (116) (15.2g, 0.05 mol) in pyridine-acetic acid (100 ml, 3:1 v/v) was refluxed for 4h to afford **ketone (133)** (11.8g, 88%). Spectroscopic data were identical with the material described previously (Chapter 6.2.11.7).

6.2.14.1 9-Thio-10-(1,3-dithiole-2-ylidene)-9,10-dihydro-anthracene (138)

A stirred mixture of ketone (132) (440 mg, 1.5 mmol) and phosphorus pentasulphide (450 mg, 1 mmol) in pyridine (15 ml) was refluxed for 2h. After cooling, the mixture was filtered, the solvent evaporated *in vacuo*, water (25 ml) added and the mixture extracted with dichloromethane (3 x 30 ml). The combined extracts were washed sequentially with (i) 20% sodium hydroxide solution (2 x 25 ml), (ii) 10% sodium chloride solution (30 ml) and (iii) water (25 ml) and then dried ($MgSO_4$), filtered and the solvent evaporated *in vacuo*. Column chromatography (silica, 15 x 2 cm) of the residue, eluting with cyclohexane-toluene (5:1 v/v), afforded **compound (138)** (350 mg, 75%) as a dark-blue solid. Mpt. 215-217^{o}C; Analysis found: C, 65.4; H, 2.9; S, 30.7; Required for $C_{17}H_{10}S_3$: C, 65.8; H, 3.2; S, 31.0%; m/e EI: 310 (M^+), CI: 311; ν_{max} (Nujol): 1590, 1255, 1195, 1090, 1085, 1015, 800, 795, 780, 705, 670, 645 cm^{-1}; λ_{max} (MeCN): 579, 366, 230 nm; δ_H ($CDCl_3$): 8.24, 7.93, 7.65 and 7.43 (each 2H,first order AMRX,all ortho J_{HH}=8Hz), 6.40 (2H,s) ppm.

6.2.14.2 9-Thio-10-(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (139)

Thioketone (139) was prepared analogously to compound (138) (Chapter 6.2.14.1). Ketone (133) (650 mg, 2 mmol) and phosphorus pentasulphide (450 mg, 1 mmol) in pyridine (50 ml) gave **compound (139)** (460 mg, 68%) as a deep-blue solid. Mpt. 214-216^{o}C; Analysis found: C, 67.6; H, 4.2; S, 28.0; Required for $C_{19}H_{14}S_3$: C, 67.4; H, 4.2; S, 28.4%; m/e EI: 338 (M^+), CI: 339; ν_{max} (Nujol): 1585, 1295, 1265, 1200, 1195,

1150, 1080, 1010, 810, 780, 750, 720, 645 cm^{-1}; λ_{max} (MeCN): 598, 332, 230, 192 nm; δ_H ($CDCl_3$): 8.23, 7.84, 7.58 and 7.36 (each 2H,first order AMRX,all ortho J_{HH}=8Hz), 1.96 (6H,s) ppm.

6.2.15 2-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-1,3-indandione (143)

A stirred mixture of 1,3-indandione (142) (5g, 0.04 mol) and sodium ethoxide [from sodium (0.9g, 0.04 mol)] in dry ethanol (100 ml) was refluxed for 0.5h under nitrogen. Methiodide salt (116) (11.7g, 0.04 mol) was added as a suspension in dry ethanol (20 ml) and the mixture refluxed for a further 4h. After cooling, the solvent was evaporated *in vacuo*, water (100 ml) added and the residue extracted with dichloromethane (3 x 75 ml). The combined extracts were dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Column chromatography (silica, 15 x 2 cm) of the residue, eluting with dichloromethane, afforded **compound (143)** (9.8g, 90%) as a bright yellow solid. Mpt. >250°C; Analysis found: C, 61.5; H, 3.8; S, 23.0; Required for $C_{14}H_{10}O_2S_2$: C, 61.3; H, 3.7; S, 23.4%; m/e EI: 274 (M^+), CI: 275; ν_{max} (Nujol): 1705, 1585, 1525, 1370, 1340, 1270, 1250, 1210, 1160, 955, 845, 825, 765, 735, 700, 680, 650 cm^{-1}; λ_{max} (MeCN): 411, 235 nm; δ_H ($CDCl_3$): 7.76 and 7.58 (each 2H, AA'XX'), 2.31 (6H,s) ppm; δ_C [$CDCl_3$,$Cr(acac)_3$]: 187.4, 166.6, 140.2, 133.2, 129.3, 121.8, 113.5, 13.0 ppm.

6.2.16 2-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-1,3-indandithione (144)

A stirred mixture of compound (143) (150 mg, 0.95 mmol) and phosphorus pentasulphide (180 mg, 0.4 mmol) in dry toluene, or benzene (75 ml) was refluxed under nitrogen for 3h. After cooling, the mixture was filtered, the solvent evaporated *in vacuo*, water (50 ml) added and

the mixture extracted with dichloromethane (3 x 75 ml). The combined extracts were washed sequentially with (i) 20% sodium hydroxide (2 x 50 ml), (ii) 10% sodium chloride solution (25 ml) and (iii) water (30 ml) and then dried ($MgSO_4$), filtered and the solvent evaporated *in vacuo*. Column chromatography (silica, 30 x 2 cm) of the residue, eluting with cyclohexane-dichloromethane (3:1 v/v), afforded **compound (144)** (135 mg, 80%) as a black solid. Mpt. 191-193^{o}C; Analysis found: C, 55.0; H, 3.5; Required for $C_{14}H_{10}S_4$: C, 54.9; H, 3.3%; m/e EI: 306 (M^+), CI: 307; ν_{max} (Nujol): 1590, 1255, 1200, 1090, 1085, 1015, 790, 780, 690 cm^{-1}; λ_{max} (MeCN): 474, 366, 329, 281 nm; δ_H ($CDCl_3$): 7.66 and 7.50 (each 2H,AA'XX'), 2.39 (4H,s) ppm.

A repeat of the above reaction in the presence of "moist" phosphorus pentasulphide eluted first **compound (144)** (17 mg, 10%) and then **compound (X)** (121 mg, 80%) as a deep-red solid. Mpt. 237-242^{o}C; Analysis found: C, 60.9; H, 4.4; S, 3.1; Required for $C_{14}H_{12}S_3$: C, 60.8; H, 4.4; S, 3.4%; m/e EI: 276 (M^+), CI: 277; ν_{max} (Nujol): 1600, 1580, 1365, 1330, 1320, 1260, 1200, 1050, 840, 770, 720 cm^{-1}; λ_{max} (MeCN): 505, 364, 381 nm; δ_H ($CDCl_3$): 7.93 (1H,d), 7.47 (1H,d), 7.40 (2H,m), 3.79 (2H,s), 2.28 (3H,s), 2.24 (3H,s) ppm; δ_C [$CDCl_3$,$Cr(acac)_3$]: 202.3, 157.8, 147.8, 143.8, 131.7, 131.0, 128.5, 127.5, 125.0, 124.5, 124.2, 38.5, 13.7, 13.1 ppm.

6.2.17 Conversion of Dithione (144) to Diketone (143)

A mixture of compound (144) (100 mg, 0.33 mmol) and mercury(II) acetate (318 mg, 1.0 mmol) in acetic acid-chloroform (1:1 v/v) (50 ml) was stirred at 20^{o}C for 2h. The organic layer was separated and washed sequentially with (i) 10% sodium bicarbonate solution (3 x 50 ml) and

(ii) water (3 x 50 ml), dried ($MgSO_4$), filtered and the solvent evaporated *in vacuo*. Column chromatography (silica, 10 x 1 cm) of the residue, eluting with dichloromethane, afforded **compound (143)** (77 mg, 85%). The product was identical in all respects with that described in Chapter 6.2.15.

6.2.18.1 2-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-1,3-indandione-7,7,8,8-tetracyano-p-quinodimethane complex (1:1 stoichiometry) (143a)

A boiling solution of compound (143) (100 mg, 0.36 mmol) in dry acetonitrile (20 ml) was added to a boiling solution of TCNQ (1) (75 mg, 0.36 mmol) in dry acetonitrile (10 ml) and the resultant green solution refluxed for 0.5h under nitrogen. After cooling to 20°C, the solid was collected by filtration, washed with ice-cold acetonitrile (2 x 10 ml) and dried *in vacuo* to afford **complex (143a)** (128 mg, 74%) as a light green solid. Mpt. >250°C; Analysis found: C, 65.4; H, 3.1; N, 11.4; Required for $C_{26}H_{14}N_4O_2S_2$ (*ie.* a 1:1 complex): C, 65.3; H, 2.9; N, 11.7%; ν_{max} (Nujol): 3030, 2200, 1645, 1575, 1535, 1480, 1350, 1335, 1220, 1200, 845, 745, 735, 730 cm^{-1}.

6.2.18.2 2-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-1,3-indandithione-7,7,8,8-tetracyano-p-quinodimethane complex (1:1 stoichiometry) (144a)

Complex (144a) was prepared analogously to complex (143a) (Chapter 6.2.18.1). Compound (144) (75 mg, 0.25 mmol) and TCNQ (1) (51 mg, 0.25 mmol) in dry acetonitrile (30 ml) yielded **complex (144a)** (76 mg, 60%) as a black powder. Mpt. *ca.* 210°C (dec); Analysis found: C, 60.7; H, 2.5:

N, 11.4; Required for $C_{26}H_{14}N_4S_4$ (*ie.* a 1:1 complex): C, 61.1; H, 2.8; N, 11.0%; ν_{max} (Nujol): 2200, 1580, 1255, 1090, 1015, 710, 650 cm^{-1}.

6.3 EXPERIMENTAL TO CHAPTER 3

6.3.1 Materials

1-Selena-3-thiolium tetrafluoroborate (153) was prepared in three steps following the literature procedure from 1-selena-3-thiole-2-thione (157)[144], (85% yield). Mpt. 70-72°C; δ_H (CF_3CO_2H): 12.41 (1H,s), 10.15 and 9.53 (each 1H,AB J=6Hz) ppm [lit.[141] Mpt. not given; δ_H (CF_3CO_2H): 12.43 (1H,s), 10.18 and 9.48 (each 1H,AB J=6Hz) ppm].

6.3.2 2-Dimethoxyphosphinyl-1-selena-3-thiole (151)

Following the procedure detailed for ester (100) (Chapter 6.2.10.1) freshly-distilled trimethylphosphite (0.25 ml, 2 mmol), sodium iodide (300 mg, 2 mmol) and cation (153) (475mg, 2 mmol) were stirred in dry acetonitrile (50 ml) under nitrogen for 2h. Column chromatography (neutral alumina, 6 x 2 cm), eluting with ethyl acetate under a flow of nitrogen, afforded **ester (151)** (471 mg, 91%) as a deep-red oil that decomposed in air. Analysis found: C, 22.8; H, 3.3; Required for $C_5H_9O_3PSSe$: C, 23.2; H, 3.5%; m/e EI: 260 (M^+), CI: 261; ν_{max} (neat): 3000, 2940, 2900, 2840, 1670, 1550, 1310, 1240(br), 1180, 1030(br), 970, 900, 820, 770, 745 cm^{-1}; δ_H ($CDCl_3$): 6.67 and 6.43 (each 1H,AB J=8Hz), 5.26 (1H,d,J=4.5Hz), 3.81 (6H,d,J=10Hz) ppm.

6.3.3 Wittig-Horner Reactions of 2-dimethoxyphosphinyl-1-selena-3-thiole (151)

These reactions were carried out using the general procedure described in Chapter 6.2.11.1.

6.3.3.1 2-Cyclopentylidene-1-selena-3-thiole (163)

Cyclopentanone (0.05 ml, 0.6 mmol) in dry THF (5 ml) was added to a solution of carbanion (162) [from ester (151) (155 mg, 0.6 mmol) and n-BuLi (1.6 M, 0.4 ml, 0.65 mmol)] in dry THF (50 ml) at -78^{o}C. Column chromatography (silica, 20 x 2 cm), eluting with hexane-toluene (1:1 v/v) afforded **compound (163)** (95 mg, 71%) as a yellow semi-solid. Analysis found: C, 44.7; H, 4.8; Required for $C_8H_{10}SSe$: C, 44.2; H, 4.6%; m/e EI: 218 (M^+), CI: 219; ν_{max} (neat): 3025, 1580, 1535, 1130, 980, 870, 810, 790, 650 cm^{-1}; δ_H ($CDCl_3$): 6.52 and 6.37 (each 1H,AB, J=8Hz), 2.32-2.19 (4H,m), 1.71-1.66 (4H,m) ppm; δ_C ($CDCl_3$): 147.8, 126.7, 119.4, 110.8, 34.2, 30.8, 26.8, 28.3 ppm.

6.3.3.2 2-Cyclohexylidene-1-selena-3-thiole (164)

Cyclohexanone (0.072 ml, 0.7 mmol) in dry THF (5 ml) was added to a solution of carbanion (162) [from ester (151) (180 mg, 0.7 mmol) and n-BuLi (1.6 M, 0.47 ml, 0.75 mmol)] in dry THF (50 ml) at -78^{o}C. Column chromatography (silica, 20 x 2 cm) eluting with hexane-toluene (1:1 v/v) afforded **compound (164)** (115 mg, 71%) as a yellow semi-solid. Analysis found: C, 46.5; H, 4.9; Required for $C_9H_{12}SSe$: C, 46.8; H, 5.2%; m/e EI: 232 (M^+), CI: 233; ν_{max} (neat): 3025, 1590, 1520, 1270, 1090, 870, 650 cm^{-1}; δ_H ($CDCl_3$): 6.51 and 6.43 (each 1H,AB J=8Hz), 2.74 (2H,t,J=7.5

Hz), 1.71-1.67 (4H,m), 1.49-1.40 (4H,m) ppm; δ_C ($CDCl_3$): 143.7, 127.3, 118.0, 112.6, 36.2, 32.8, 30.3, 26.9, 22.6 ppm.

6.3.3.3 2-(Diphenylmethylene)-1-selena-3-thiole (165)

Benzophenone (73 mg, 0.4 mmol) in dry THF (5 ml) was added to a solution of carbanion (162) [from ester (151) (105 mg, 0.4 mmol) and n-BuLi (1.6 M, 0.28 ml, 0.45 mmol)] in dry THF (50 ml) at -78°C. Column chromatography (silica, 15 x 2 cm), eluting with toluene, afforded **compound (165)** (77 mg, 61%) as a light orange solid. Mpt. 61-63°C; Analysis found: C, 61.0; H, 3.7; Required for $C_{16}H_{12}SSe$: C, 60.9; H, 3.8%; m/e EI: 316 (M^+), CI: 317; ν_{max} (Nujol): 3020, 1585, 1510, 1270, 1250, 1130, 1020, 790, 710, 650 cm^{-1}; δ_H ($CDCl_3$): 7.30-7.13 (10H,m), 6.56 and 6.44 (each 1H,AB J=6Hz) ppm; δ_C ($CDCl_3$): 141.4, 139.9, 129.6, 128.2, 127.7, 127.0, 125.5, 123.0, 122.3 ppm.

6.3.3.4 2-Benzylidene-1-selena-3-thiole (166)

Benzaldehyde (42 mg, 0.4 mmol) in dry THF (5 ml) was added to a solution of carbanion (162) [from ester (151) (105 mg, 0.4 mmol) and n-BuLi (1.6 M, 0.28 ml, 0.45 mmol)] in dry THF (50 ml) at -78°C. Column chromatography (silica, 25 x 2 cm), eluting with carbon tetrachloride afforded **compound (166)** (55 mg, 58%) as a yellow solid. Mpt. 52-55°C; Analysis found: C, 50.3; H, 3.3; Required for $C_{10}H_8SSe$: C, 50.2; H, 3.4%; m/e EI: 240 (M^+), CI: 241; ν_{max} (Nujol): 1590, 1525, 1500, 1305, 1275, 1160, 1150, 1035, 850, 800, 640 cm^{-1}; δ_H ($CDCl_3$): 7.63-7.40 (5H,m), 6.61 (1H,s), 6.49 and 6.37 (2H,AB J=6Hz) ppm.

6.3.3.5 Cis/Trans-9,10-bis(1-selena-3-thiole-2-ylidene)-9,10-dihydroanthracene (167)

A suspension of anthraquinone (155 mg, 0.75 mmol) in dry THF (15 ml) was added to a solution of carbanion (162) [from ester (151) (390 mg, 1.5 mmol) and n-BuLi (1.6 M, 1.0 ml, 1.6 mmol)] in dry THF (100 ml) at -78^{o}C. Column chromatography (silica, 30 x 2 cm), eluting with cyclohexane-toluene (3:1 v/v), afforded **compound (167)** (225 mg, 63%) as a dark orange solid. Mpt. >240^{o}C; Analysis found: C, 50.4; H, 2.5; S, 13.0; Required for $C_{20}H_{12}S_2Se_2$: C, 50.6; H, 2.6; S, 13.5%; m/e DEI: 476 (M^+), DCI: 477; ν_{max} (Nujol): 3030, 1595, 1520, 1495, 1310, 1280, 1260, 850, 765, 735, 670, 640 cm^{-1}; λ_{max} (MeCN): 409, 377, 265, 236 nm; δ_H ($CDCl_3$): 7.67-7.19 (16H,m), 6.79 and 6.60 (each 1H, AB, J=7.1Hz), 6.71 and 6.50 (each 1H,AB J=6.7Hz).

Continued elution with dichloromethane yielded unreacted anthraquinone (20 mg, 13%) followed by a second product. Recrystallisation from dichloromethane afforded an analytically pure sample of **9-oxo-10-(1-selena-3-thiole-2-ylidene)-9,10-dihydroanthracene (168)** (25 mg, 10%) as a red solid. Mpt. 189-192^{o}C; Analysis found: C, 59.6; H, 3.2; Required for $C_{17}H_{10}OSSe$: C, 59.8; H, 3.0%; m/e EI: 342 (M^+), CI: 343; ν_{max} (Nujol): 2840, 1640, 1590, 1325, 1300, 1295, 1265, 1165, 1090, 930, 760, 720, 685, 630 cm^{-1}; λ_{max} (MeCN): 465, 362, 246, 200 nm; δ_H ($CDCl_3$): 7.97, 7.83, 7.67 and 7.48 (each 2H,first order AMRX), 6.83 and 6.57 (each 1H, AB J=7Hz) ppm.

Reaction of ketone (168) (275 mg, 0.8 mmol) in dry THF (10 ml) with a solution of carbanion (162) [from ester (151) (210 mg, 0.8 mmol) and n-BuLi (1.6 M, 0.56 ml, 0.9 mmol)] in dry THF (50 ml) at -78^{o}C also

afforded **compound (167)** (285 mg, 75%). Spectroscopic data was identical with the material described above.

6.3.3.6 9-(1,3-Dithiole-2-ylidene)-10-(1-selena-3-thiole-2-ylidene)-9,10-dihydroanthracene (169)

Ketone (132) (235 mg, 0.8 mmol) in dry THF (10 ml) was added to a solution of carbanion (162) [from ester (151) (210 mg, 0.8 mmol) and n-BuLi (1.6 M, 0.56 ml, 0.9 mmol)] in dry THF (50 ml) at -78^{o}C. Column chromatography (silica, 25 x 2 cm), eluting with cyclohexane-toluene (3:1 v/v), afforded **compound (169)** (198 mg, 58%) as an orange solid. Mpt. >240^{o}C; Analysis found: C, 56.0; H, 2.7; S, 22.9; Required for $C_{20}H_{12}S_3Se$: C, 56.2; H, 2.8; S, 22.5%; m/e DEI: 428 (M^+), DCI: 429; ν_{max} (Nujol): 1585, 1520, 1270, 1150, 1120, 1090, 1010, 960, 850 cm^{-1}; λ_{max} (MeCN): 419, 365, 240 nm; δ_H ($CDCl_3$): 7.73-7.60 (4H,m), 7.34-7.20 (4H, m), 6.79 and 6.55 (each 1H,AB J=7Hz), 6.30 (2H,s) ppm.

6.3.3.7 9-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-10-(1-selena-3-thiole-2-ylidene)-9,10-dihydroanthracene (170)

Ketone (133) (248 mg, 0.8 mmol) in dry THF (10 ml) was added to a solution of carbanion (162) [from ester (151) (210 mg, 0.8 mmol) and n-BuLi (1.6 M, 0.56 ml, 0.9 mmol)] in dry THF (50 ml) at -78^{o}C. Column chromatography (silica, 25 x 2 cm), eluting with cyclohexane-toluene (3:1 v/v), afforded **compound (170)** (248 mg, 68%) as an orange solid. Mpt. >240^{o}C; Analysis found: C, 58.2; H, 3.7; S, 20.7; Required for $C_{22}H_{16}S_3Se$: C, 58.0; H, 3.5; S, 21.1%; m/e DEI: 456 (M^+), DCI: 457; ν_{max} (Nujol): 1590, 1540, 1250, 1130, 1090, 1005, 970, 890, 775, 750 cm^{-1};

λ_{max} (MeCN): 427, 362, 242 nm; δ_H ($CDCl_3$): 7.72-7.59 (4H,m), 7.31-7.26 (4H,m), 6.78 and 6.54 (each 1H,AB J=7Hz), 1.94 (6H,s) ppm.

6.3.4 Alternative Synthesis of 9-oxo-10-(1-selena-3-thiole-2-ylidene)-9,10-dihydroanthracene (168)

Ketone (168) was best prepared following the procedure detailed for compound (132) (Chapter 6.2.14.1); a mixture of anthrone (5g, 0.026 mol), methiodide salt (160) (9.4g, 0.03 mol) in pyridine-acetic acid (3:1 v/v, 50 ml) was refluxed for 8h to afford **ketone (168)** (7.6g, 86%). Analytical data were identical with the sample described previously (Chapter 6.3.3.5).

6.4 EXPERIMENTAL TO CHAPTER 4

6.4.1 Materials

Tetrathiafulvalenyllithium (monolithio-TTF) (175) was prepared according to the literature[154] from TTF (2) (1.0g, 4.9 mmol) and LDA [from n-BuLi (1.6M, 3.25 ml, 5.2 mmol) and diisopropylamine (0.68 ml, 4.9 mmol)] in dry ether and used immediately in further reactions, where indicated.

4-(1-Oxooctadecyl)tetrathiafulvalene (71b) was prepared according to the literature procedure from monolithio-TTF (175) and octadecanoyl-chloride (30% yield). Mpt. 84-85°C (lit.[105] not given).

4-(Carboxy)tetrathiafulvalene (182) was prepared following the literature procedure from monolithio-TTF (175) and solid carbon dioxide (50% yield). Mpt. 180-182°C (dec) [lit.[154] 182-184°C (dec)].

4-Chlorocarbonyltetrathiafulvalene (186) was prepared following the literature procedure from TTF-carboxylic acid (182) and oxalyl chloride (65% yield). Mpt. 127-134°C (dec) [lit.[157] 130-135°C (dec)].

6.4.2 4-(1-Thiooctadecyl)tetrathiafulvalene (176)

To a stirred solution of ketone (71b) (70 mg, 0.15 mmol) in dry benzene (30 ml) under nitrogen was added Lawesson's reagent (40 mg. 0.1 mmol) and the mixture heated at reflux for 1h. After cooling, water (30 ml) was added and the mixture extracted into toluene-petroleum ether (b.p. 40-60°C) (3:1 v/v, 3 x 25 ml). The combined extracts were washed sequentially with 50 ml portions of (i) 20% sodium chloride solution, (ii) 5% sodium carbonate solution, and (iii) water, and then dried ($MgSO_4$), filtered and the solvent evaporated *in vacuo*. Column chromatography (silica, 20 x 1 cm), of the residue, eluting with cyclohexane-toluene (10:1 v/v) afforded **thione (176)** (36 mg, 50%) as a deep-blue solid. TLC analysis [silica, cyclohexane-toluene (10:1 v/v)] showed the sample to be pure, although satisfactory microanalytical data could not be obtained. Mpt. 71-76°C; Analysis found: C, 57.9; H, 6.8; Required for $C_{24}H_{38}S_5$: C, 59.2; H, 7.9%; High Resolution MS found: 486.15789; Required: 486.15771; ν_{max} (Nujol): 3030, 1590, 1560, 1300, 1260, 1180, 1120, 1045, 1020, 930, 800, 760 cm^{-1}.

6.4.3 4-(1-Hydroxyoctadecyl)tetrathiafulvalene (178)

Zinc dust (200 mg, 3 mmol) and mercury(II) chloride (27mg, 0.1 mmol) were stirred together for 0.5h in a mixture of water (10 ml) and hydrochloric acid (conc., 3 ml) at 20°C; the solution was decanted and immediately re-covered with water (5 ml) and hydrochloric acid (conc.,

5 ml). To the Zn-Hg amalgam was added ketone (71b) (70 mg, 0.15 mmol) in benzene (20 ml) and the mixture vigorously stirred under reflux for 2h. The mixture was decanted and extracted into toluene (2 x 20 ml), washed with water (5 x 20 ml), dried ($MgSO_4$), filtered and the solvent evaporated *in vacuo*. Column chromatography (silica, 12 x 1 cm) of the residue, eluting with cyclohexane-acetone (1:1 v/v) gave first, unreacted starting material (71b) (15 mg, 21%) and then **alcohol (178)** (35 mg, 50%) as a yellow solid. Mpt. 31-33^{o}C; Analysis found: C, 60.1; H, 8.2; Required for $C_{24}H_{40}OS_4$: C, 61.0; H, 8.5%; m/e EI: 472 (M^+), CI: 474; ν_{max} (Nujol): 3400-3150 (br), 3030, 1260, 795, 720, 645 cm^{-1}. No mass spectral or TLC evidence was obtained for the formation of the desired product (177) in the crude reaction mixture.

6.4.4 4-(Carbomethoxy)tetrathiafulvalene (183)

This preparation is representative of the esters prepared by acid catalysed esterification. A suspension of acid (182) (50 mg, 0.2 mmol) in methanol (15 ml) and sulphuric acid (conc., 1 ml) was refluxed for 2h. After cooling, the solvent was removed *in vacuo*, water (30 ml) was added and the residue extracted into dichloromethane (3 x 30 ml). The combined extracts were washed sequentially with (i) 10% sodium carbonate solution (3 x 30 ml), (ii) 10% sodium chloride solution (30 ml), and (iii) water (30 ml), dried ($MgSO_4$), filtered and the solvent evaporated *in vacuo*. Column chromatography (silica, 10 x 1 cm) of the residue, eluting with cyclohexane-toluene (1:1 v/v), afforded **compound (183)** (35 mg, 68%) as a red solid. Mpt. 88-89^{o}C; Analysis found: C, 37.0; H, 2.5; Required for $C_8H_6O_2S_4$: C, 36.6; H, 2.3%; m/e EI: 262 (M^+), CI: 263; ν_{max} (Nujol): 3035, 1700, 1290, 800, 720, 690, 650 cm^{-1}; δ_H ($CDCl_3$): 7.35 (1H,s), 6.28 (2H,s), 3.81 (3H,s) ppm.

6.4.5 4-(Carboethoxy)tetrathiafulvalene (181)

Ester (181) was prepared following the procedure described for compound (183) (Chapter 6.4.4). Acid (182) (50 mg, 0.2 mmol) in ethanol (15 ml) and sulphuric acid (conc., 1 ml) for 2h at reflux gave **compound (181)** (35 mg, 64%) as a red solid. Mpt. 80-82^{o}C (lit.: 79.5-80.5^{o}C, prepared from monolithio-TTF). Analysis found: C, 38.9; H, 2.8; Required for $C_9H_8O_2S_4$: C, 39.1; H, 2.9%; m/e EI: 276 (M^+), CI: 277; ν_{max} (Nujol): 3025, 1695, 1300, 1285, 1245, 1190, 1035, 790 cm^{-1}; δ_H ($CDCl_3$): 7.28 (1H,s), 6.31 (2H,s), 4.25 (2H,q,J=6.8 Hz), 1.38 (3H,t,J=6.8 Hz) ppm.

6.4.6 4-(Carbohexoxy)tetrathiafulvalene (184)

6.4.6.1 By Acid-Catalysed Esterification

Following the procedure described for ester (183) (Chapter 6.4.4), acid (182) (75 mg, 0.3 mmol) in 1-hexanol (5 ml) and sulphuric acid (conc., 1 ml) for 18h at reflux gave **compound (184)** (6 mg, 6%) as a red solid. Mpt. 61-64^{o}C; Analysis found: C, 47.4; H, 5.3; Required for $C_{13}H_{16}O_2S_4$: C, 47.0; H, 4.9%; High Resolution MS found: 332.00351; Required: 332.00332; ν_{max} (Nujol): 3030, 1705, 1290, 1285, 1235, 1200, 1030, 800, 690 cm^{-1}.

6.4.6.2 By Reaction of Acid Chloride (186) and 1-Hexanol

A solution of acid chloride (186) (53 mg, 0.2 mmol) in dry dichloromethane (5 ml) and a solution of dry pyridine (0.02 ml, 0.25 mmol) in dry dichloromethane (5 ml) were added dropwise, separately and simultaneously, to a stirred solution of 1-hexanol (0.025 ml, 0.2 mol)

in dry dichloromethane (10 ml) at 0°C under nitrogen over a period of 0.5h. The mixture was stirred for 12h at 20°C, the solvent evaporated *in vacuo*, and ether (15 ml) added. The solution was filtered and the solvent again evaporated *in vacuo*. Column chromatography (silica. 5 x 1 cm) of the residue, eluting with cyclohexane-toluene (1:1 v/v), afforded **compound** (184) (12 mg, 18%). The product was identical in all respects with the sample described above (Chapter 6.4.6.1).

6.4.7 4-(Carbooctoxy)tetrathiafulvalene (185)

6.4.7.1 By Acid-Catalysed Esterification

Following the procedure described for ester (183) (Chapter 6.4.4), acid (182) (75 mg, 0.3 mmol) in 1-octanol (5 ml) and sulphuric acid (conc., 1 ml) for 204h at reflux gave **compound (185)** (5 mg, 4%) as a red powder. Mpt. 60-62°C; Analysis found: C, 49.7; H, 5.9; Required for $C_{15}H_{20}O_2S_4$: C, 50.0; H, 5.6%; High Resolution MS found: 360.02839; Required: 360.03461; ν_{max} (Nujol): 3025, 1700, 1300, 1280, 1240, 1195, 1045, 800, 780, 650 cm^{-1}.

6.4.7.2 By Reaction of Monolithio-TTF (175) with Octylchloroformate (187)

A solution of compound (187) (1.9g, 10 mmol) in dry ether (10 ml) was syringed into a stirring slurry of monolithio-TTF (175) at -78°C. The mixture was stirred at -78°C for 2h, slowly warmed to 20°C over a period of 12h, water (75 ml) added and the mixture stirred for a further 1h at 20°C. The mixture was extracted with ether (3 x 100 ml) the combined extracts washed sequentially with (i) 10% sodium chloride

solution (3 x 75 ml) and (ii) water (3 x 75 ml), dried ($MgSO_4$), filtered and the solvent evaporated *in vacuo*. Column chromatography (silica, 20 x 4.5 cm) of the residue, eluting with hexane-toluene (3:1 v/v), followed by column chromatography (neutral alumina, 20 x 4.5 cm), eluting with hexane-toluene (4:1 v/v), afforded crude product (185). Three recrystallisations from methanol-ether (5:1 v/v) yielded analytically pure **compound (185)** (618 mg, 35%) as red crystals. The product was identical in all respects with the sample described above (Chapter 6.4.7.1).

6.4.8 Hexadecylchloroformate (189)

A solution of pyridine (1.2 ml, 15 mmol) in dry ether (5 ml) was added dropwise to a stirred solution of triphosgene (188) (1.3g, 5 mmol) and 1-hexadecanol (3.6g, 15 mmol) in dry ether (75 ml) under nitrogen at 0^oC; the resulting mixture was stirred for 2h at 0^oC during which time a heavy white solid precipitated. The solid was removed by filtration and the filtrate evaporated *in vacuo*. Vacuum distillation of the residue afforded the **product (189)** (3.8g, 84%) as a clear thick oil. Bpt. 138-144^oC (1 mm Hg); ν_{max} (neat): 2920, 2850, 1780, 1460, 1380, 1260, 1150, 945, 840, 720, 690 cm^{-1}.

6.4.9 4-(Carbohexadecoxy)tetrathiafulvalene (190)

Ester (190) was prepared following the procedure described for compound (185) (Chapter 6.4.7.3). A solution of compound (189) (3.0g, 10 mmol) in dry ether (10 ml) was added to a stirring slurry of monolithio-TTF (175) at -78^oC. Work-up afforded the crude product (190) (670 mg, 29%). Recrystallisation from methanol yielded **compound** (190b)

as an orange solid. Mpt. 72°C (phase change at 45-55°C); Analysis found: C, 58.1; H, 7.3; S, 27.0; Required for $C_{23}H_{36}O_2S_4$: C, 58.4: H. 7.7; S, 27.1%; High Resolution MS found: 472.15566; Required: 472.15786; m/e EI: 472 (M^+), CI: 473; ν_{max} (Nujol): 3030, 2960, 2920, 2850, 1720, 1480, 1472, 1305, 1290, 1280, 1265 cm^{-1}.

Recrystallisation from toluene yielded **compound (190a)** as a red solid. Mpt. 71-72°C; Analysis found: C, 58.7; H, 7.8; S, 27.2; Required for $C_{23}H_{36}O_2S_4$: C, 58.4; H, 7.7; S, 27.1%; High Resolution MS found: 472.15376; Required: 472.15786; m/e EI: 472 (M^+), CI: 473; ν_{max} (KBr): 3030, 2960, 2920, 2855, 1700, 1305, 1290, 1275, 1250, 1195, 1050, 800, 720, 650 cm^{-1}; λ_{max} (CH_2Cl_2): 435, 317, 235 nm.

6.4.10 Hexadecylchlorothionoformate (193)

A solution of pyridine (1.2 ml, 15 mmol) in dry ether (5 ml) was added dropwise to a stirred solution of freshly-distilled thiophosgene (2.5g, 25 mmol) and 1-hexadecathiol (3.9g, 15 mmol) in dry ether (75 ml) under nitrogen at 0°C; the resulting mixture was stirred for 2h, during which time a white solid precipitated. The solid was removed by filtration and the filtrate evaporated *in vacuo*. Vacuum distillation of the residue afforded **compound (193)** (3.6g, 72%) as an off-white solid which solidified on standing. Mpt. *ca.* 20°C; Bpt. 152-155°C (1 mm Hg). ν_{max} (neat): 2920, 2860, 1460, 1380, 1270, 1025, 720 cm^{-1}.

6.4.11 4-(Thiocarbohexadecoxy)tetrathiafulvalene (191)

Thioester (191) was prepared following the procedure described for compound (185) (Chapter 6.4.7.3). A solution of compound (193) (3.2g. 10 mmol) in dry ether (10 ml) was added to a stirring slurry of mono-lithio-TTF (175) at -78°C. Work-up afforded **compound (191)** (908 mg. 38%) as a deep-purple solid. Mpt. 78-80°C; Analysis found: C, 56.5; H, 7.4; S, 32.8; Required for $C_{23}H_{36}OS_5$: C, 56.5; H, 7.4; S, 32.8%; High Resolution MS found: 488.13488; Required: 488.13697; m/e EI: 488 (M^+), CI: 489; ν_{max} (Nujol): 3030, 2910, 2850, 1508, 1475, 1285, 1270, 1235, 1205, 1045, 895, 830, 815, 800, 720, 635 cm^{-1}; λ_{max} (CH_2Cl_2): 539, 309 nm.

6.5 EXPERIMENTAL TO CHAPTER 5

6.5.1 Reagents

1-Methyl-1,4-dithiacyclohexanium (MDT), *1-methylthiacyclohexanium (MPMS)* and *1-methylthiacyclopentanium (MTMS)* iodide salts, (202), (203) and (204), respectively, were prepared following the literature procedures by treatment of the appropriate sulphide (0.05 mol) with an excess of methyl iodide, and were isolated as white needle-crystals in quantitative yield. Mpt. 169-170°C (lit.[167], not given), 174-176°C (lit.[168] 138-139°C) and 202-205°C (lit.[168] 127-128°C), respectively.

6.5.2 1-Methyl-1,4-dithiacyclohexanium-7,7,8,8-tetracyano-p-quinodimethane salt, MDT(TCNQ)$_2$ (205)

A boiling solution of MDT iodide (202) (105 mg, 0.4 mmol) in dry acetonitrile (*ca.* 15 ml) was added to a boiling solution of TCNQ (1) (163 mg, 0.8 mmol) in dry acetonitrile (*ca.* 15 ml) and the resultant dark-green solution refluxed for 0.5h under nitrogen. After slow cooling to -5^{o}C, the shiny, blue-black platelets that formed were filtered, washed with cold acetonitrile (2 x 5 ml) and dried *in vacuo* to yield **salt (205)** (190 mg, 71%). Mpt. 230-232^{o}C (dec); Analysis found: C, 64.5; H, 3.4; N, 20.3; S, 12.1; Required for $C_{29}H_{19}N_8S_2$ (*ie.* a 1:2 complex): C, 64.1; H, 3.5; N, 20.6; S, 11.8%; ν_{max} (KBr,FT-IR): 2198, 2179, 2167, 1553, 1511, 1409, 1331, 1315, 1131, 951, 898, 697 cm^{-1}; λ_{max} (MeCN): 843, 744, 344 nm; λ_{max} (Nujol): 2340, 1040, 920, 665, 400 nm.

Crystals of salt (205) suitable for X-ray analysis were grown using the slow diffusion method. MDT iodide (202) (30 mg, 0.11 mmol) and TCNQ (1) (30 mg, 0.15 mmol) were placed in separate compartments of an H-cell diffusion apparatus (volume 40 ml) and dry acetonitrile (*ca.* 35 ml) added under nitrogen. After 432h at -10^{o}C, the crystals formed were collected and dried in air to afford **salt (205)** (20 mg, 40%).

6.5.3 1-Methylthiacyclohexanium-7,7,8,8-tetracyano-p-quinodimethane salt, MPMS(TCNQ)$_2$ (206)

This salt was prepared in the same manner as salt (205) (Chapter 6.5.2). MPMS iodide (203) (73 mg, 0.3 mmol) and TCNQ (1) (123 mg, 0.6 mmol) yielded blue-black needles of **salt (206)** (122 mg, 62%). Mpt. 246-247^{o}C (dec); Analysis found: C, 68.0; H, 3.9; N, 21.4; S, 6.2; Required

for $C_{30}H_{21}N_8S$ (*ie.* a 1:2 complex): C, 68.5; H, 4.0; N. 21.3; S. 6.1%: ν_{max} (KBr,FT-IR): 2199, 2180, 2160, 1563, 1517, 1503, 1441, 1416, 1329, 1126, 953, 880, 832, 692 cm^{-1}; λ_{max} (MeCN): 843, 744, 394, 246 nm; λ_{max} (Nujol): 2330, 1025, 880, 645, 395 nm.

6.5.4 1-Methylthiapentanium-7,7,8,8-tetracyano-p-quinodimethane salt, MTMS$(TCNQ)_2$ (207)

This salt was prepared in the same manner as salt (205) (Chapter 6.5.2). MTMS iodide (204) (115 mg, 0.5 mmol) and TCNQ (1) (204 mg, 1 mmol) yielded shiny blue-black needles of **salt (207)** (191 mg, 60%). Mpt. 232-235^{o}C (dec); Analysis found: C, 67.8; H, 3.9; N, 21.5; S, 6.2; Required for $C_{29}H_{19}N_8S$ (*ie.* a 1:2 salt): C, 68.1; H, 3.7; N, 21.9; S, 6.3%; ν_{max} (KBr,FT-IR): 2196, 2179, 2166, 1576, 1543, 1506, 1404, 1333, 1180, 861, 823 cm^{-1}; λ_{max} (MeCN): 843, 744, 394, 200 nm; λ_{max} (Nujol): 2290, 1025, 900, 670, 400 nm.

In all cases, the salts (205)-(207) were isolated in best yields by mixing the respective methiodide salts and TCNQ in a 1:2 molar ratio in hot acetonitrile as described above. Salts (205)-(207) with the same stoichiometry were also obtained by mixing methiodide salts and TCNQ in other molar ratios (*eg.* 2:1, 1:1, 1:4) in hot acetonitrile. Analytical and spectroscopic data of salts then obtained were consistent with salts (205)-(207) described above.

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APPENDIX I

X-RAY CRYSTAL DATA

I.1 Crystal Data for 9,10-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (127)

Chemical Formula: $C_{24}H_{20}S_4$; $\underline{M}_r$ = 436.64; crystal system = monoclinic; space group = $P2_1/c$; a = 9.007(1) Å, b = 12.719(1) Å, c = 19.332(2) Å; α = 90.00(0)°, β = 99.44(0)°, γ = 90.00(0)°; U = 2184.68 (3) $Å^3$; Z = 4; F(000) = 912; Mo-Kα radiation (graphite monochromator), λ = 0.71069 Å; μ (Mo-Kα) = 68.6 cm^{-1}, D_c = 1.328 g cm^{-3}; 3027 independent reflections, of which 1336, with $I > 2\sigma(I)$, were used; 253 parameters refined; R = 0.0823, R_w = 0.0628.

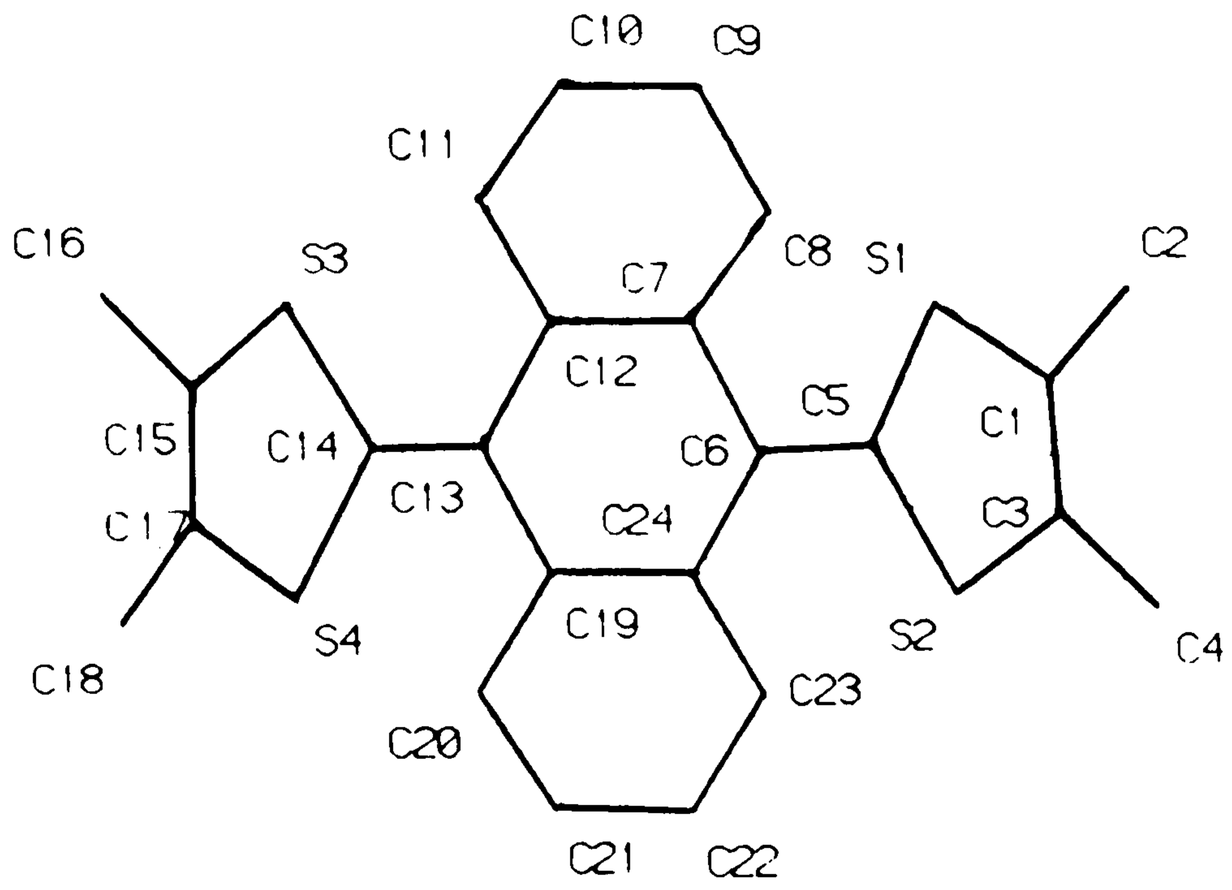

Figure A.1: *Atom numbering scheme for compound (127).*

Data were collected on a CAD 4 diffractometer following previously described procedures. The structure was solved by direct methods (SHELX 84) and developed and refined using standard Fourier and least-squares procedures. Non-hydrogen atoms were refined anisotropically, hydrogens isotropically. Bond lengths and angles are given in Table A.1.

C(1)-S(1)	1.759(11)	S(1)-C(1)-C(2)	117.3(8)
C(1)-C(2)	1.507(15)	S(1)-C(1)-C(3)	115.5(8)
C(1)-C(3)	1.342(15)	C(2)-C(1)-C(3)	127.2(10)
C(3)-S(2)	1.770(11)	S(2)-C(3)-C(1)	116.6(9)
C(3)-C(4)	1.542(15)	S(2)-C(3)-C(4)	116.2(8)
C(5)-S(1)	1.744(10)	C(1)-C(3)-C(4)	127.0(10)
C(5)-S(2)	1.755(10)	S(1)-C(5)-S(2)	111.6(5)
C(5)-C(6)	1.362(14)	S(1)-C(5)-C(6)	124.6(8)
C(6)-C(7)	1.492(14)	S(2)-C(5)-C(6)	123.6(8)
C(6)-C(24)	1.485(16)	C(5)-C(6)-C(7)	119.6(10)
C(7)-C(8)	1.386(17)	C(5)-C(6)-C(24)	125.1(9)
C(7)-C(12)	1.425(16)	C(7)-C(6)-C(24)	115.1(9)
C(8)-C(9)	1.439(16)	C(6)-C(7)-C(8)	121.5(10)
C(9)-C(10)	1.433(19)	C(6)-C(7)-C(12)	115.9(10)
C(10)-C(11)	1.417(19)	C(8)-C(7)-C(12)	122.6(10)
C(11)-C(12)	1.448(15)	C(7)-C(8)-C(9)	119.7(11)
C(12)-C(13)	1.458(17)	C(8)-C(9)-C(10)	118.5(11)
C(13)-C(14)	1.323(17)	C(9)-C(10)-C(11)	121.8(10)
C(13)-C(19)	1.482(14)	C(10)-C(11)-C(12)	118.5(11)
C(14)-S(3)	1.766(11)	C(7)-C(12)-C(11)	118.7(11)
C(14)-S(4)	1.760(11)	C(7)-C(12)-C(13)	119.2(9)
C(15)-S(3)	1.834(15)	C(11)-C(12)-C(13)	122.1(10)
C(15)-C(16)	1.539(17)	C(12)-C(13)-C(14)	124.1(10)
C(15)-C(17)	1.337(17)	C(12)-C(13)-C(19)	114.4(10)
C(17)-S(4)	1.802(11)	C(14)-C(13)-C(19)	121.3(10)
C(17)-C(18)	1.493(19)	S(3)-C(14)-S(4)	110.4(7)
C(19)-C(20)	1.421(16)	S(3)-C(14)-C(13)	125.6(9)
C(19)-C(24)	1.412(16)	S(4)-C(14)-C(13)	123.7(8)
C(20)-C(21)	1.430(15)	S(3)-C(15)-C(16)	113.5(9)
C(21)-C(22)	1.388(18)	S(3)-C(15)-C(17)	116.6(10)
C(22)-C(23)	1.383(17)	C(16)-C(15)-C(17)	129.8(13)
C(23)-C(24)	1.427(15)	S(4)-C(17)-C(15)	114.1(10)
		S(4)-C(17)-C(18)	117.1(8)
		C(15)-C(17)-C(18)	128.7(11)
		C(13)-C(19)-C(20)	122.7(10)
		C(13)-C(19)-C(24)	118.1(10)
		C(20)-C(19)-C(24)	119.1(9)
		C(19)-C(20)-C(21)	117.2(10)
		C(20)-C(21)-C(22)	122.9(11)
		C(21)-C(22)-C(23)	120.0(10)
		C(22)-C(23)-C(24)	118.7(11)
		C(6)-C(24)-C(19)	117.1(9)
		C(6)-C(24)-C(23)	120.9(10)
		C(19)-C(24)-C(23)	121.9(10)
		C(1)-S(1)-C(5)	98.4(5)
		C(3)-S(2)-C(5)	97.3(5)
		C(14)-S(3)-C(15)	97.5(5)
		C(14)-S(4)-C(17)	99.9(6)

Table A.1: *Bond lengths (Å) and angles (°) for compound (127) See Figure A.1 for numbering scheme.*

I.2 Crystal Data for 9,10-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene-7,7,8,8-tetracyano-p-quinodimethane complex, (127a)

Chemical Formula: $C_{24}H_{20}S_4^{2+}(C_{12}H_4N_4)_4^{2-}$; M_r = 1253.4; crystal system = triclinic; space group = $P\bar{1}$; a = 6.725(1) Å, b = 15.035(3) Å, c = 15.537(3) Å; α = 8.38(2)°, β = 83.16(1)°, γ = 87.15(1)°; U = 1537.1 Å^3; D_c = 1.354 g cm^{-3}; Z = 1; F(000) = 644; Cu-Kα radiation (graphite monochromator), λ = 1.54184 Å; μ (Cu-Kα) = 1.85 mm^{-1}, 3600 unique reflections were measured, of which 2593, with $I > 4\sigma(I)$ were used in subsequent refinement; 416 parameters refined; R = 0.048, R_w = 0.052.

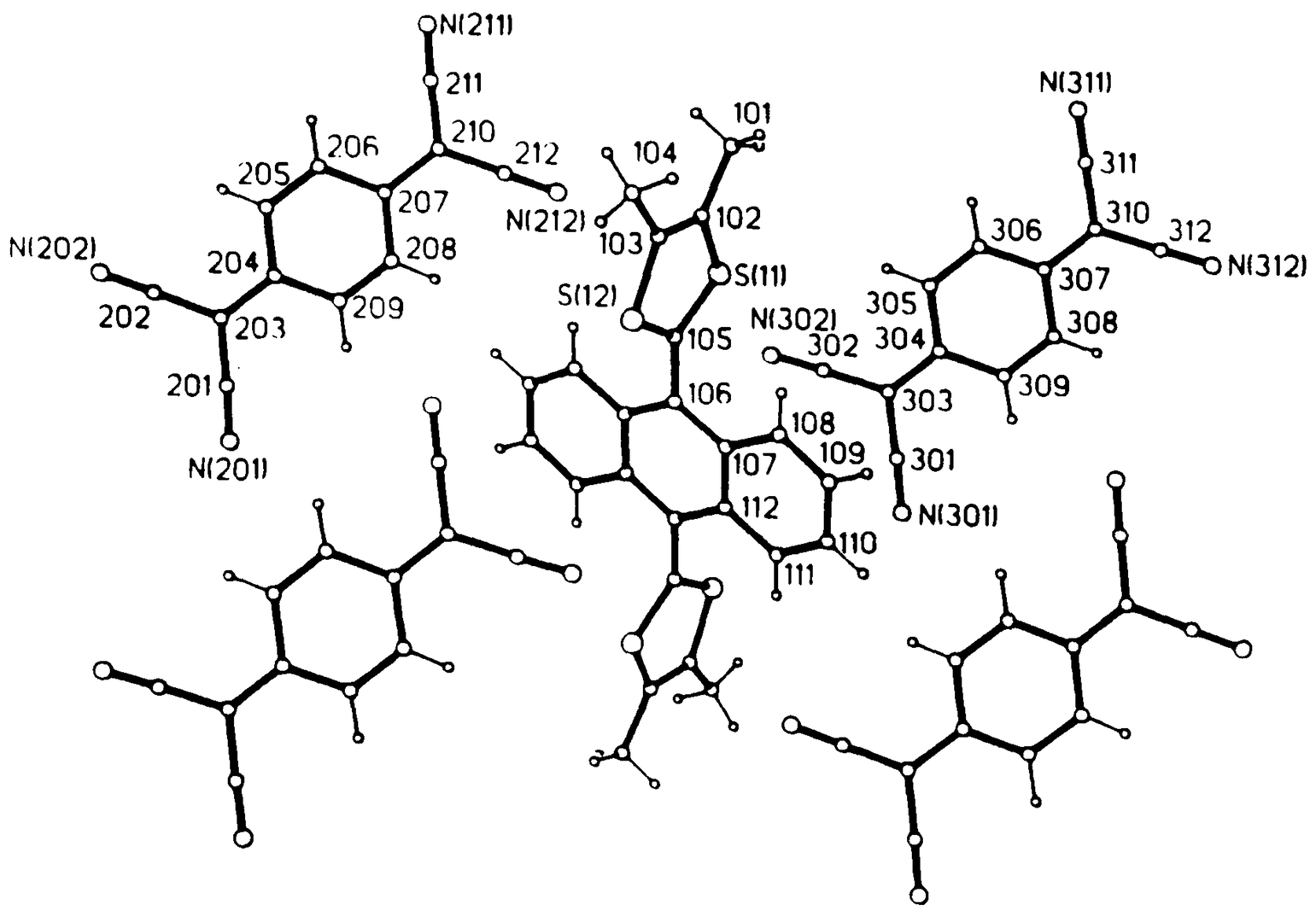

Figure A.2: *Atom numbering scheme for compound (127a).*

Data were collected on a Stoe-Siemans diffractometer using a variable width w scan. The structure was solved by direct methods (SHELX 85) and difference syntheses. Non-hydrogen atoms were refined anisotropically, all hydrogens placed in calculated positions [C-H = 0.96Å, $\hat{HCH}$ = 109.5°(CH_3)]. Bond lengths and angles are given in Table A.2.

S(11)-C(102)	1.709(4)	S(11)-C(105)-S(12)	114.6(2)
S(11)-C(105)	1.668(3)	S(11)-C(105)-C(106)	122.4(3)
S(12)-C(103)	1.713(4)	S(12)-C(105)-C(106)	122.9(2)
S(12)-C(105)	1.663(4)	C(105)-C(106)-C(107)	118.8(3)
C(101)-C(102)	1.504(6)	C(105)-C(106)-C(112)	119.2(3)
C(102)-C(103)	1.339(5)	C(107)-C(106)-C(112)	121.9(3)
C(103)-C(104)	1.487(6)	C(106)-C(107)-C(108)	122.2(3)
C(105)-C(106)	1.487(5)	C(106)-C(107)-C(112)	119.1(3)
C(106)-C(107)	1.405(5)	C(108)-C(107)-C(112)	118.7(3)
C(106)-C(112)	1.401(5)	C(107)-C(108)-C(109)	119.9(4)
C(107)-C(108)	1.427(5)	C(108)-C(109)-C(110)	121.4(4)
C(107)-C(112)	1.429(5)	C(109)-C(110)-C(111)	121.2(4)
C(108)-C(109)	1.364(6)	C(110)-C(111)-C(112)	120.1(3)
C(109)-C(110)	1.383(6)	C(107)-C(112)-C(111)	118.7(3)
C(110)-C(111)	1.361(5)	C(107)-C(112)-C(106)	119.0(3)
C(111)-C(112)	1.427(5)	C(111)-C(112)-C(106)	122.3(3)
C(201)-C(203)	1.417(6)	C(203)-C(201)-N(201)	179.3(4)
C(201)-N(201)	1.147(6)	C(203)-C(202)-N(202)	178.7(5)
C(202)-C(203)	1.439(5)	C(201)-C(203)-C(202)	115.6(3)
C(202)-N(202)	1.140(6)	C(201)-C(203)-C(204)	122.9(3)
C(203)-C(204)	1.401(5)	C(202)-C(203)-C(204)	121.4(4)
C(204)-C(205)	1.422(5)	C(203)-C(204)-C(205)	121.4(3)
C(204)-C(209)	1.425(5)	C(203)-C(204)-C(209)	121.2(3)
C(205)-C(206)	1.358(5)	C(205)-C(204)-C(209)	117.4(3)
C(206)-C(207)	1.428(5)	C(204)-C(205)-C(206)	121.1(3)
C(207)-C(208)	1.420(5)	C(205)-C(206)-C(207)	121.4(4)
C(207)-C(210)	1.413(5)	C(206)-C(207)-C(208)	117.2(3)
C(208)-C(209)	1.355(5)	C(206)-C(207)-C(210)	121.3(3)
C(210)-C(211)	1.412(6)	C(208)-C(207)-C(210)	121.5(3)
C(210)-C(212)	1.428(6)	C(207)-C(208)-C(209)	121.5(3)
C(211)-N(211)	1.155(7)	C(204)-C(209)-C(208)	121.3(3)
C(212)-N(212)	1.142(6)	C(207)-C(210)-C(211)	121.8(3)
C(301)-C(303)	1.430(6)	C(207)-C(210)-C(212)	122.0(4)
C(301)-N(301)	1.148(6)	C(211)-C(210)-C(212)	116.1(3)
C(302)-C(303)	1.436(6)	C(210)-C(211)-N(211)	177.8(4)
C(302)-N(302)	1.140(5)	C(210)-C(212)-N(212)	179.5(5)
C(303)-C(304)	1.384(5)	C(303)-C(301)-N(301)	177.4(5)
C(304)-C(305)	1.423(5)	C(303)-C(302)-N(302)	178.0(4)
C(304)-C(309)	1.440(5)	C(301)-C(303)-C(302)	115.5(3)
C(305)-C(306)	1.339(5)	C(301)-C(303)-C(304)	122.0(4)
C(306)-C(307)	1.435(5)	C(302)-C(303)-C(304)	122.4(4)
C(307)-C(308)	1.435(5)	C(303)-C(304)-C(305)	121.5(3)
C(307)-C(310)	1.374(5)	C(303)-C(304)-C(309)	120.7(3)
C(308)-C(309)	1.345(5)	C(305)-C(304)-C(309)	117.8(3)
C(310)-C(311)	1.430(6)	C(304)-C(305)-C(306)	121.1(4)
C(310)-C(312)	1.443(5)	C(305)-C(306)-C(307)	121.6(4)
C(311)-N(311)	1.134(6)	C(306)-C(307)-C(308)	117.4(3)
C(312)-N(312)	1.142(5)	C(306)-C(307)-C(310)	121.3(3)
		C(308)-C(307)-C(310)	121.3(3)
C(102)-S(11)-C(105)	97.0(2)	C(307)-C(308)-C(309)	121.0(3)
C(103)-S(12)-C(105)	97.7(2)	C(304)-C(309)-C(308)	121.0(4)
S(11)-C(102)-C(101)	118.0(3)	C(307)-C(310)-C(311)	121.7(4)
S(11)-C(102)-C(103)	116.1(3)	C(307)-C(310)-C(312)	123.5(4)
C(101)-C(102)-C(103)	125.9(4)	C(311)-C(310)-C(312)	114.8(3)
S(12)-C(103)-C(102)	114.5(3)	C(310)-C(311)-N(311)	179.3(4)
S(12)-C(103)-C(104)	118.6(3)	C(310)-C(312)-N(312)	178.6(4)
C(102)-C(103)-C(104)	126.9(3)		

Table A.2: *Bond lengths (Å) and angles (^{o}) for complex (127a) See Figure A.2 for numbering scheme.*

I.3 Crystal Data for 1-Methyl-1,4-dithiacyclohexanium-7,7,8,8-tetracyano-p-quinodimethane salt, MDT(TCNQ)$_2$ (205)

Chemical Formula: $(C_5H_{11}S_2)^+ 2(C_{12}H_4N_4)^{\frac{1}{2}-}$; M_r = 543.64; crystal system = triclinic; space group = $P\bar{1}$; a = 7.970(4) Å, b = 13.010(2) Å, c = 14.169(2) Å; α = 68.28(1)°, β = 93.48(3)°, γ = 86.90(4)°; U = 1357.7 (7) Å^3; Z = 2; F(000) = 562; Mo-Kα radiation (graphite monochromator), λ = 0.71069 Å; μ (Mo-Kα) = 110.7 cm^{-1}, D_c = 1.330 g cm^{-3}; 4785 independent reflections, of which 3026, with $I > 1.5\sigma(I)$, were used: 355 parameters refined; R = 0.060, R_w = 0.059.

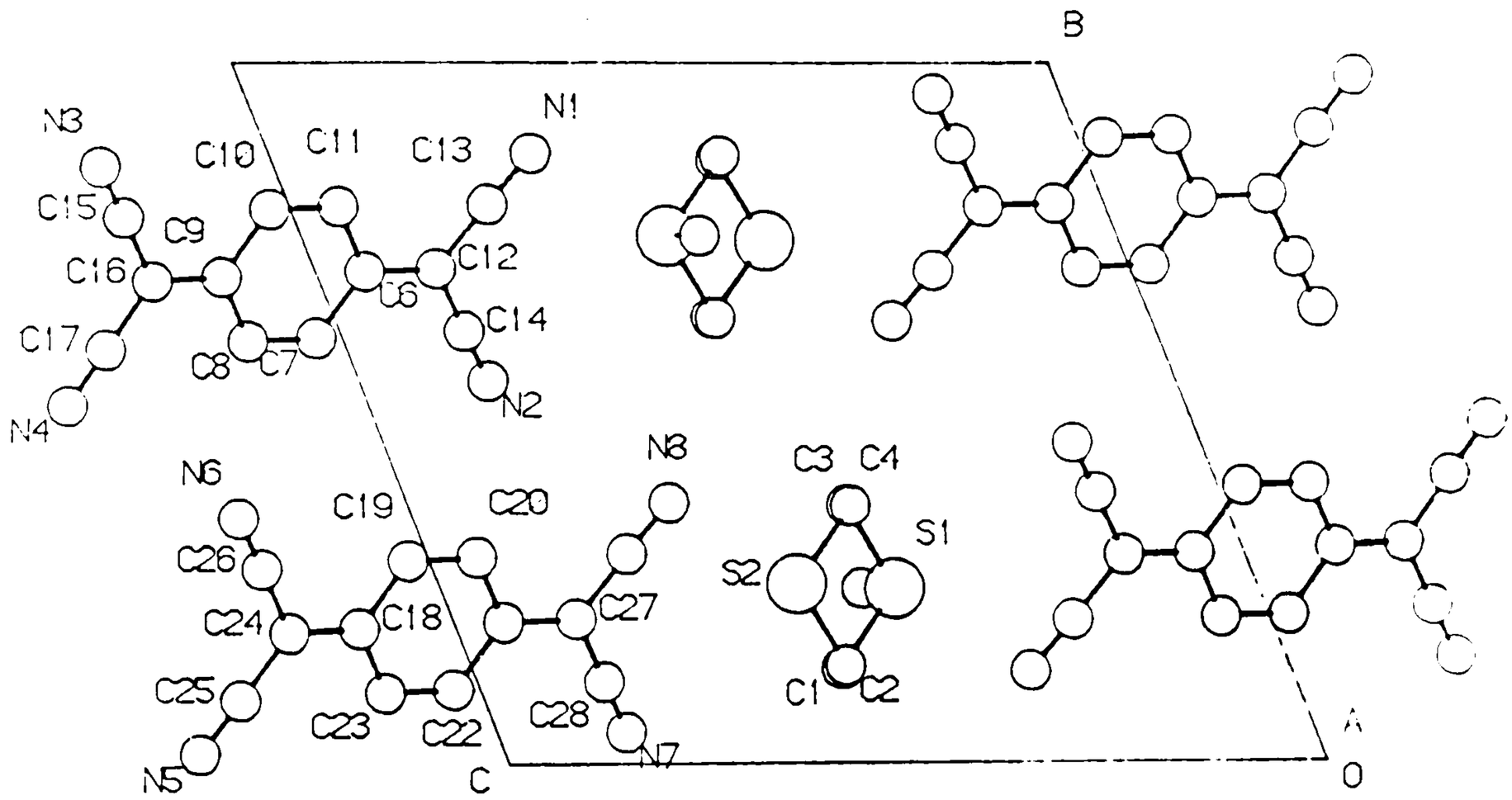

Figure A.3: *View along crystallographic a-axis of MDT(TCNQ)$_2$ (205); atom numbering scheme.*

Data were collected on a CAD 4 diffractometer following previously described procedures. The structure was solved by direct methods (SHELX 84). Non-hydrogen atoms were refined anisotropically, all hydrogens atoms placed in calculated positions (C-H = 0.96 Å, U = 0.10 Å^2). Bond lengths and angles are given in Table A.3.

C(1)-S(1)	1.797(6)	C(4)-S(1)-C(1)	102.5(3)
C(1)-C(2)	1.512(8)	C(5)-S(1)-C(1)	102.4(3)
C(2)-S(2)	1.793(7)	C(5)-S(1)-C(4)	101.8(3)
C(3)-S(2)	1.795(7)	C(3)-S(2)-C(2)	99.7(3)
C(3)-C(4)	1.521(8)	C(2)-C(1)-S(1)	110.7(4)
C(4)-S(1)	1.794(6)	C(1)-C(2)-S(2)	113.7(4)
C(5)-S(1)	1.761(7)	C(4)-C(3)-S(2)	113.4(4)
C(6)-C(7)	1.434(6)	C(3)-C(4)-S(1)	110.6(4)
C(6)-C(11)	1.430(6)	C(11)-C(6)-C(7)	117.7(4)
C(6)-C(12)	1.388(6)	C(12)-C(6)-C(7)	121.3(4)
C(7)-C(8)	1.352(6)	C(12)-C(6)-C(11)	121.0(5)
C(8)-C(9)	1.431(6)	C(8)-C(7)-C(6)	121.1(4)
C(9)-C(10)	1.434(6)	C(9)-C(8)-C(7)	121.4(4)
C(9)-C(15)	1.389(6)	C(10)-C(9)-C(8)	117.7(4)
C(10)-C(11)	1.357(6)	C(16)-C(9)-C(8)	121.3(4)
C(12)-C(13)	1.422(7)	C(16)-C(9)-C(10)	121.0(4)
C(12)-C(14)	1.428(6)	C(11)-C(10)-C(9)	121.0(4)
C(13)-N(1)	1.151(6)	C(10)-C(11)-C(6)	121.2(5)
C(14)-N(2)	1.145(6)	C(13)-C(12)-C(6)	121.8(4)
C(15)-C(16)	1.421(6)	C(14)-C(12)-C(6)	122.8(5)
C(15)-C(17)	1.422(6)	C(14)-C(12)-C(13)	115.3(4)
C(16)-N(3)	1.147(6)	C(12)-C(13)-N(1)	178.5(5)
C(17)-N(4)	1.152(6)	C(12)-C(14)-N(2)	178.9(5)
C(18)-C(19)	1.430(6)	C(16)-C(15)-C(9)	122.5(5)
C(18)-C(23)	1.429(6)	C(17)-C(15)-C(9)	121.9(4)
C(18)-C(24)	1.398(6)	C(17)-C(15)-C(16)	115.6(4)
C(19)-C(20)	1.356(6)	C(15)-C(16)-N(3)	179.5(4)
C(20)-C(21)	1.435(6)	C(15)-C(17)-N(4)	179.7(4)
C(21)-C(22)	1.429(6)	C(23)-C(18)-C(19)	117.7(4)
C(21)-C(29)	1.396(6)	C(24)-C(18)-C(19)	121.2(4)
C(22)-C(23)	1.350(6)	C(24)-C(18)-C(23)	121.1(4)
C(24)-C(25)	1.420(6)	C(20)-C(19)-C(18)	121.0(4)
C(24)-C(26)	1.427(6)	C(21)-C(20)-C(19)	121.2(5)
C(25)-N(5)	1.144(6)	C(22)-C(21)-C(20)	117.5(4)
C(26)-N(6)	1.153(6)	C(27)-C(21)-C(20)	120.7(4)
C(27)-C(28)	1.425(6)	C(27)-C(21)-C(22)	121.8(4)
C(27)-C(29)	1.422(7)	C(23)-C(22)-C(21)	121.3(4)
C(28)-N(7)	1.147(6)	C(22)-C(23)-C(18)	121.3(4)
C(29)-N(8)	1.149(6)	C(25)-C(24)-C(18)	122.1(4)
		C(26)-C(24)-C(18)	122.0(5)
		C(26)-C(24)-C(25)	115.9(4)
		C(24)-C(25)-N(5)	178.8(5)
		C(24)-C(26)-N(6)	179.1(4)
		C(28)-C(27)-C(21)	122.4(5)
		C(29)-C(27)-C(21)	121.1(4)
		C(29)-C(27)-C(28)	116.4(4)
		C(27)-C(28)-N(7)	179.6(3)
		C(27)-C(29)-N(8)	178.2(5)

Table A.3: *Bond lengths (Å) and angles (°) for MDT(TCNQ)$_2$ (205); See Figure A.3 for numbering scheme.*

APPENDIX II

PUBLICATIONS

Parts of the work contained in this thesis have been reported in the following publications:

1. "*The Preparation of New Bis(1,3-Dithiole) Derivatives: Extended π-Donors for Organic Metals*". M.R. Bryce and A.J. Moore, *Tetrahedron Lett.*, 29, 1075 (1988).

2. "*A New Highly-Conjugated TTF Analogue: Synthesis, Electrochemistry and a Conducting TCNQ Complex of 9,10-anthracenediylidene-2,2'-bis(4,5-dimethyl-1,3-dithiole)*". M.R. Bryce and A.J. Moore, *Synth. Met.*, 25, 203 (1988).

3. "*Magnetic Properties and Structure of MDT(TCNQ)$_2$*". S.D. Obertelli, R.H. Friend, M.R. Bryce, A.J. Moore and P. Bates, *Synth. Met.*, 27, B327 (1988).

4. "*Highly-Conjugated Bis(1,3-Dithiole) Donors*". M.R. Bryce and A.J. Moore, *Synth. Met.*, 27, B557 (1988).

5. "*Conducting Salts of Cyclic Sulphonium Cations with TCNQ: X-Ray Crystal Structure of 1-Methyl-1,4-dithianium TCNQ salt, (MDT)$^+$ (TCNQ)$_2^-$*". M.R. Bryce, A.J. Moore, P.A. Bates, M.B. Hursthouse, Z.-X. Liu and M.J. Nowak, *J.Chem.Soc.Chem.Comm.*, 1441 (1988).

6. "*Organic Metals: Synthesis and Solid-State Properties of New Extended Tetrathiafulvalene and Selenatrithiafulvalene Derivatives*". M.R. Bryce and A.J. Moore, *Pure Appl.Chem.*, in press.

APPENDIX III

LECTURES, COLLOQUIA AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate research thesis contain an appendix listing:

1. All research colloquia, research seminars and lectures arranged by the Department of Chemistry and the Chemical Society during the period of residence as a postgraduate student (* - indicates those Colloquia attended by the author)

2. All research conferences attended, and papers presented by the authors, during the period when the research for the thesis was carried out.

III.1 Lectures and Colloquia Organised by the Department of Chemistry

DURING THE PERIOD OCTOBER 1986 - SEPTEMBER 1987

* ALLEN, Prof. Sir G. (Unilever Research) Biotechnology and the Future of the Chemical Industry	13th November 1986
BARTSCH, Dr. B. (University of Sussex) Low Co-ordinated Phosphorus Compounds	6th May 1987
BLACKBURN, Dr. M. (University of Sheffield) Phosphonates as Analogues of Biological Phosphate Esters	27th May 1987
* BORDWELL, Prof. F.G.(Northeastern University,USA) Carbon Anions, Radicals, Radical Anions and Radical Cations	9th March 1987
CANNING, Dr. N.D.S. (University of Durham) Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis	26th November 1986
CANNON, Dr. R.D. (University of East Anglia) Electron Transfer in Polynuclear Complexes	11th March 1987
CLEGG, Dr. W. (University of Newcastle-upon-Tyne) Carboxylate Complexes of Zinc; Charting a Structural Jungle	28th January 1987
* DÖPP, Prof. D. (University of Duisburg) Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes	5th November 1986
DORFMÜLLER, Prof. T. (University of Bielefeld) Rotational Dynamics in Liquids and Polymers	8th December 1986

	GOODGER, Dr. E.M. (Cranfield Inst.Technology) Alternative Fuels for Transport	12th March 1987
*	GREENWOOD, Prof. N.N. (University of Leeds) Glorious Gaffes in Chemistry	16th October 1986
	HARMER, Dr. M. (I.C.I. Chemicals & Polymer Group) The Role of Organometallics in Advanced Materials	7th May 1987
*	HUBBERSTEY, Dr. P. (University of Nottingham) Demonstration Lecture on Various Aspects of Alkali Metal Chemistry	5th February 1987
*	HUDSON, Prof. R.F. (University of Kent) Aspects of Organophosphorus Chemistry	17th March 1987
	HUDSON, Prof. R.F. (University of Kent) Homolytic Rearrangements of Free Radical Stability	18th March 1987
	JARMAN, Dr. M. (Institute of Cancer Research) The Design of Anti Cancer Drugs	19th February 1987
	KRESPAN, Dr. C. (E.I. Dupont de Nemours) Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry	26th June 1987
*	KROTO, Prof. H.W. (University of Sussex) Chemistry in Stars, between Stars and in the Laboratory	23rd October 1986
*	LEY, Prof. S.V. (Imperial College) Fact and Fantasy in Organic Synthesis	5th March 1987
*	MILLER, Dr. J. (Dupont Central Research, USA) Molecular Ferromagnets; Chemistry and Physical Properties	3rd December 1986
	MILNE/CHRISTIE, Dr.A./Mr.S.(International Paints) Chemical Serendipity: A Real Life Case Study	20th November 1986
	NEWMAN, Dr. R. (University of Oxford) Change and Decay: A Carbon-13 CP/MAS NMR Study of humification and Coalification Processes	4th March 1987
	OTTEWILL, Prof. R.H. (University of Bristol) Colloid Science a Challenging Subject	22nd January 1987
	PASYNKIEWICZ, Prof. S. (Technical Univ.,Warsaw) Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium	11th May 1987
*	ROBERTS, Prof. S.M. (University of Exeter) Synthesis of Novel Antiviral Agents	24th June 1987

RODGERS, Dr. P.J. (I.C.I. Billingham) — 12th February 1987
Industrial Polymers from Bacteria

SCROWSTON, Dr. R.M. (University of Hull) — 6th November 1986
From Myth and Magic to Modern Medicine

SHEPHERD, Dr. T. (University of Durham) — 11th February 1987
Pteridine Natural Products; Synthesis and Use in Chemotherapy

THOMSON, Prof. A. (University of East Anglia) — 4th February 1987
Metalloproteins and Magneto-optics

* WILLIAMS, Prof. R.L. (Metropolitan Police Forensic Science) — 27th November 1987
Science and Crime

WONG, Prof.E.H. (University of New Hampshire,USA) — 29th October 1986
Coordination Chemistry of P-O-P Ligands

WONG, Prof.E.H. (University of New Hampshire,USA) — 17th February 1987
Symmetrical Shapes from Molecules to Art and Nature

DURING THE PERIOD OCTOBER 1987 - SEPTEMBER 1988

* BAILEY, Dr. P.D. (University of York) — November 1987
Oncogenes

* BIRCHALL, Prof. D. (I.C.I. Advanced Materials) — 25th April 1988
Environment Chemistry of Aluminium

* BORER, Dr. K. (University of Durham Industrial Research Laboratories) — 18th February 1988
The Brighton Bomb - (A Forensic Science View)

BOSSONS, L. (Durham Chemistry Teachers' Centre) — 16th March 1988
GCSE Practical Assessment

* BUTLER, Dr. A.R. (University of St.Andrews) — 5th November 1987
Chinese Alchemy

* CAIRNS-SMITH, Dr. A. (Glasgow University) — 28th January 1988
Clay Minerals and the Origin of Life

DAVIDSON, Dr. J. (Herriot-Watt University) — November 1987
Metal Promoted Oligomerisation Reactions of Alkynes

* GRAHAM, Prof. W.A.G. (University of Alberta, Canada) — 3rd March 1988
Rhodium and Iridium Complexes in the Activation of Carbon-Hydrogen Bonds

* GRAY, Prof. G.W. (University of Hull) — 22nd October 1987
Liquid Crystals and their Applications

* HARTSHORN, Prof. M.P. (University of Canterbury, New Zealand) — 7th April 1988
Aspects of Ipso-Nitration

HOWARD, Dr. J. (I.C.I. Wilton) — 3rd December 1987
Chemistry of Non-Equilibrium Processes

JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) — 29th June 1988
GCSE Chemistry Post-mortem

JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) — 6th July 1988
GCE Chemistry A-Level Post-mortem

* KOCH, Prof. H.F. (Ithaca College, U.S.A.) — 7th March 1988
Does the E2 Mechanism Occur in Solution ?

LACEY, Mr. (Durham Chemistry Teacher's Centre) — 9th February 1988
Double Award Science

* LUDMAN, Dr. C.J. (Durham University) — 10th December 1987
Explosives

McDONALD, Dr. W.A. (I.C.I. Wilton) — 11th May 1988
Liquid Crystal Polymers

MAJORAL, Prof. J.-P. (Université Paul Sabatier) — 8th June 1988
Stabilisation by Complexation of Short-Lived Phosphorus Species

MAPLETOFT, Mrs. M. (Durham Chemistry Teachers' Centre) — 4th November 1987
Salters' Chemistry

NIETO DE CASTRO, Prof. C.A. (University of Lisbon and Imperial College) — 18th April 1988
Transport Properties of Non-Polar Fluids

* OLAH, Prof. G.A. (University of Southern California) — 29th June 1988
New Aspects of Hydrocarbon Chemistry

* PALMER, Dr. F. (University of Nottingham) — 21st January 1988
Luminescence (Demonstration Lecture)

PINES, Prof. A. (University of California, Berkeley, U.S.A.) — 28th April 1988
Some Magnetic Moments

RICHARDSON, Dr. R. (University of Bristol) — 27th April 1988
X-Ray Diffraction from Spread Monolayers

ROBERTS, Mrs. E. (SATRO Officer for Sunderland) — 13th April 1988
Talk - Durham Chemistry Teachers' Centre - "Links between Industry and Schools"

ROBINSON, Dr. J.A. (University of Southampton) — 27th April 1988
Aspects of Antibiotic Biosynthesis

* ROSE, van Mrs. S. (Geological Museum) — 29th October 1987
Chemistry of Volcanoes

* SAMMES, Prof. P.G. (Smith, Kline and French) — 19th December 1987
Chemical Aspects of Drug Development

* SEEBACH, Prof. D. (E.T.H. Zurich) — 12th November 1987
From Synthetic Methods to Mechanistic Insight

SODEAU, Dr. J. (University of East Anglia) — 11th May 1988
Durham Chemistry Teachers's Centre: "Spray Cans, Smog and Society"

SWART, Mr. R.M. (I.C.I.) — 16th December 1987
The Interaction of Chemicals with Lipid Bilayers

* TURNER, Prof. J.J. (University of Nottingham) — 11th February 1988
Catching Organometallic Intermediates

* UNDERHILL, Prof. A. (University of Bangor) — 25th February 1988
Molecular Electronics

* WILLIAMS, Dr. D.H. (University of Cambridge) — 26th November 1987
Molecular Recognition

* WINTER, Dr. M.J. (University of Sheffield) — 15th October 1987
Pyrotechnics (Demonstration Lecture)

DURING THE PERIOD OCTOBER 1988 - SEPTEMBER 1989

ASHMAN, Mr. A. (Durham Chemistry Teachers' Centre) — 3rd May 1989
The Chemical Aspects of the National Curriculum

AVEYARD, Dr. R. (University of Hull) — 15th March 1989
Surfactants at your Surface

AYLETT, Prof. B.J. (Queen Mary College, London) — 16th February 1989
Silicon-Based Chips: The Chemists Contribution

* BALDWIN, Prof. J.E. (Oxford University) — 9th February 1989
Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis

BALDWIN & WALKER, Drs. R.R. and R.W. (Hull University) — 24th November 1988
Combustion: Some Burning Problems

BOLLEN, Mr. F. (Durham Chemistry Teachers' Centre) — 18th October 1988
Lecture about the use of SATIS in the classroom

* BUTLER, Dr. A.R. (St. Andrews University) Cancer in Linxiam: The Chemical Dimension	15th February 1989
CADOGAN, Prof. J.I.G., (British Petroleum) From Pure Science to Profit	10th November 1988
CASEY, Dr. M. (University of Salford) Sulphoxides in Stereoselective Synthesis	20th April 1989
WALTERS & CRESSEY, Mr. D. and T. (Durham Chemistry Teachers' Centre) GCSA Chemistry 1988: "A Coroner's Report"	1st February 1989
* CRICH, Dr. D. (University College London) Some Novel Uses of Free Radicals in Organic Synthesis	27th April 1989
* DINGWALL, Dr. J. (Ciba Geigy) Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products	18th October 1988
ERRINGTON, Dr. R.J. (University of Newcastle-upon-Tyne) Polymetalate Assembly in Organic Solvents	1st March 1989
FREY, Dr. J. (Southampton University) Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl	11th May 1989
HALL, Prof. L.D. (Addenbrooke's Hospital, Cambridge) NMR - A Window to the Human Body	2nd February 1989
HARDGROVE, Dr. G. (St. Olaf College, U.S.A.) Polymers in the Physical Chemistry Laboratory	December 1988
HARWOOD, Dr. L. (Oxford University) Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry under Pressure	25th January 1988
JÄGER, Dr. C. (Friedrich-Schiller University GDR) NMR Investigations of Fast Ion Conductors of the NASICOM Type	9th December 1988
JENNINGS, Prof. R.R. (Warwick University) Chemistry of the Masses	26th January 1989
JOHNSON, Dr. B.F.G. (Cambridge University) The Binary Carbonyls	23rd February 1989
JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) Discussion Session on the National Curriculum	14th June 1989

JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) — 28th June 1989
GCSE and A Level Chemistry 1989

LUDMAN, Dr. C.J. (Durham University) — 18th October 1988
The Energetics of Explosives

MACDOUGALL, Dr. G. (Edinburgh University) — 22nd February 1989
Vibrational Spectroscopy of Model Catalytic Systems

MARKO, Dr. I. (Sheffield University) — 9th March 1989
Catalytic Asymmetric Osmylation of Olefins

McLAUCHLAN, Dr. K.A. (University of Oxford) — 16th November 1988
The Effect of Magnetic Fields on Chemical Reactions

* MOODY, Dr. C.J. (Imperial College) — 17th May 1989
Reactive Intermediates in Heterocyclic Synthesis

* MORTIMER, Dr. C. (Durham Chemistry Teachers' Centre) — 14th December 1989
The Hindenberg Disaster - an Excuse for Some Experiments

NICHOLLS, Dr. D. (Durham Chemistry Teachers' Centre) — 11th July 1989
Demo: "Liquid Air"

PAETZOLD, Prof. P. (Aachen) — 23rd May 1989
Iminoboranes XB≡NR: Inorganic Acetylenes ?

* PAGE, Dr. P.C.B. (University of Liverpool) — 3rd May 1989
Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides

POLA, Prof. J. (Czechoslovak Academy of Sciences) — 15th June 1989
Carbon Dioxide Laser Induced Chemical Reactions - New Pathways in Gas-Phase Chemistry

* REES, Prof. C.W. (Imperial College London) — 27th October 1988
Some Very Heterocyclic Compounds

REVELL, Mr. P. (Durham Chemistry Teachers' Centre) — 14th March 1989
Implementing Broad and Balanced Science 11-16

SCHMUTZLER, Prof. R. (Technische Universitat Braunschweig) — 6th October 1988
Fluorophosphines Revisited - New Contributions to an Old Theme

* SCHROCK, Prof. R.R. (M.I.T.) — 13th February 1989
Recent Advances in Living Metathesis

SINGH, Dr. G. (Teeside Polytechnic) Towards Third Generation Anti-Leukaemics	9th November 1988
* SNAITH, Dr. R. (Cambridge University) Egyptian Mummies: What, Where, Why and How ?	1st December 1988
STIBR, Dr. R. (Czechoslovak Academy of Sciences) Recent Developments in the Chemistry of Intermediate-Sited Carboranes	16th May 1989
VON RAGUE SCHLEYER, Prof. P. (Universitat Erlangen Nurnberg) The Fruitful Interplay Between Calculational and Experimental Chemistry	21st October 1988
WELLS, Prof. P.B. (Hull University) Catalyst Characterisation and Activity	10th May, 1989

III.2 Research Conferences Attended by the Author During the Period October 1986 - September 1989.

1. R.S.C. Graduate Symposium, Durham, 27th March, 1987.

2. R.S.C. Perkin Division, North East Regional Meeting, Newcastle, 15th September, 1987.

3. Autumn Meeting of R.S.C., Nottingham, 22nd - 24th September, 1987. A poster was presented entitled "*Synthesis of New Electron Donors for Organic Metals*".

4. I.R.L. Molecular Electronics Short Course, Durham, 29th - 30th September, 1987.

5. R.S.C. Graduate Symposium, Durham, 19th April, 1988.

6. International Conference on Science and Technology of Synthetic Metals (ICSM '88), Santa Fe, New Mexico, 26th June - 2nd July, 1988. A poster was presented entitled "*Highly Conjugated Bis(1,3-Dithiole) Donors*".

7. R.S.C. Perkin Division, North East Regional Meeting, York, 16th December, 1988.

8. R.S.C. Graduate Symposium, Durham, 12th April, 1989. A lecture was presented entitled "*New Organic Metals Based on Sulphur Heterocycles*".